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Heat of Mixing of Polybutadiene and Benzene

Ralph S. Jessup

Measurements have been made of the heat of mixing of polybutadiene and benzene at 26.9° C by means of a Bunsen-type calorimeter, in which diphenyl ether is the calorimetric medium. The results of these measurements can be represented by the empirical equation

$$\Delta H^M = 12.0 v_1 v_2,$$

where ΔH^M is heat of mixing in joules per cm³, and v_1 and v_2 are volume fractions of solvent and polymer, respectively. The data have been combined with previously reported data on the activity of the solvent in this system to obtain values of $\Delta\overline{S}_1$, the partial molal entropy of dilution. The curve of $\Delta\overline{S}_1/Rv_2^2$ versus v_2 for this system lies above the calculated curve of $\Delta\overline{S}_1^*/Rv_2^2$, where $\Delta\overline{S}_1^*$ is the "configurational entropy" of dilution, and also lies above the corresponding experimental curves for several other polymer-solvent systems.

1. Introduction

This paper presents results of measurements of heat of mixing of polybutadiene with benzene. These results supplement data previously reported [1] [1] on the activity of the solvent in this system. The two sets of data have been combined to yield values of partial molal entropies of dilution.

2. Materials

The sample of polybutadiene used, and its purification, including removal of solvent and permanent gases, were described in reference [1]. Reagent grade benzene was purified by fractional freezing as described previously [1, 4], and was further purified by removal of dissolved permanent gas as described in section 3.2 of this paper. The density at 25° C of the purified benzene before removal of dissolved gas was 0.87334 g/cm³, as compared with the value 0.87368 g/cm³ reported in the literature [3].

3. Apparatus and Method

3.1. Apparatus

The measurements of heat of mixing were made at 26.9° C by means of a Bunsen-type calorimeter in which diphenyl ether is the calorimetric medium. Heat absorbed in the mixing process causes partial freezing of the diphenyl ether, with a consequent change in volume. This change in volume is measured by the displacement of a mercury meniscus in a graduated capillary connected to a pool of mercury in the bottom of the calorimeter. The calorimeter has been described previously [2] and only a brief description will be given here.

The calorimeter, as used in measurements of heats of mixing of two liquids, and a buret for introducing measured quantities of one component of the mixture are shown schematically in figure 1. The mixing chamber F, the cylindrical copper pieces V, the conical copper piece K, and the connecting tubing up to a union (not shown in fig. 1) in the tube J just above K form a unit that can be lifted out of the central well of the calorimeter. This unit can be replaced by a similar unit with an electric heater for calibration purposes in place of the mixing vessel [2]. The conical copper piece K fits into a conical hole in the copper jacket cover and forms a part of this cover.

For the present measurements, the calorimeter was modified by (1) substituting a smaller buret and a smaller mixing chamber for those shown in figure 1, (2) eliminating the stirrer (Z, fig. 1), and (3) sealing off the mixing chamber at the point Y from the tube through which the stirrer shaft passes.

The buret used had a capacity of a little over 1 cm³, and could be read directly to 0.01 cm³ and by interpolation to 0.001 cm³. The mixing chamber had a capacity of 6.3 cm³. The mixing chamber also contained a shallow cup (not shown in fig. 1) into which liquid solvent admitted to the mixing chamber dropped, so that solvent came in contact with the polymer only in the gas phase.

In a measurement of heat of mixing, the solvent flows from the buret, where the volume of the liquid is measured, to the mixing chamber through the copper tube J. A part of this tube (not shown in fig. 1) is wound into a spiral and soldered to the jacket cover to insure that the liquid is at the jacket temperature before it enters the calorimeter. After leaving the spiral the liquid continues through the tubes J and L to the valve A.

The valve A (fig. 1) was originally a small needle valve, which was found to be unsuitable because appreciable and irregular quantities of heat were generated in opening and closing it. It was therefore replaced by a different type of valve illustrated in figure 2. The point of the valve needle C is enclosed in a Teflon sheath S as shown, and the pointed end of this sheath is pressed against the valve seat by a helical spring W. This spring is located in a monel metal tube M which projects above the conical copper piece K.

The upper end of the tube M is soldered to the stuffing box B (fig. 2) and its lower end is soldered to the conical copper piece K. Also soldered to the copper piece K is the monel tube L which leads to the valve A. The upper end of the spring W presses against the nut N at the bottom of the stuffing box, the nut being held in place by the force exerted by the nut H and transmitted through the packing

[1] Figures in brackets indicate the literature references at the end of this paper.

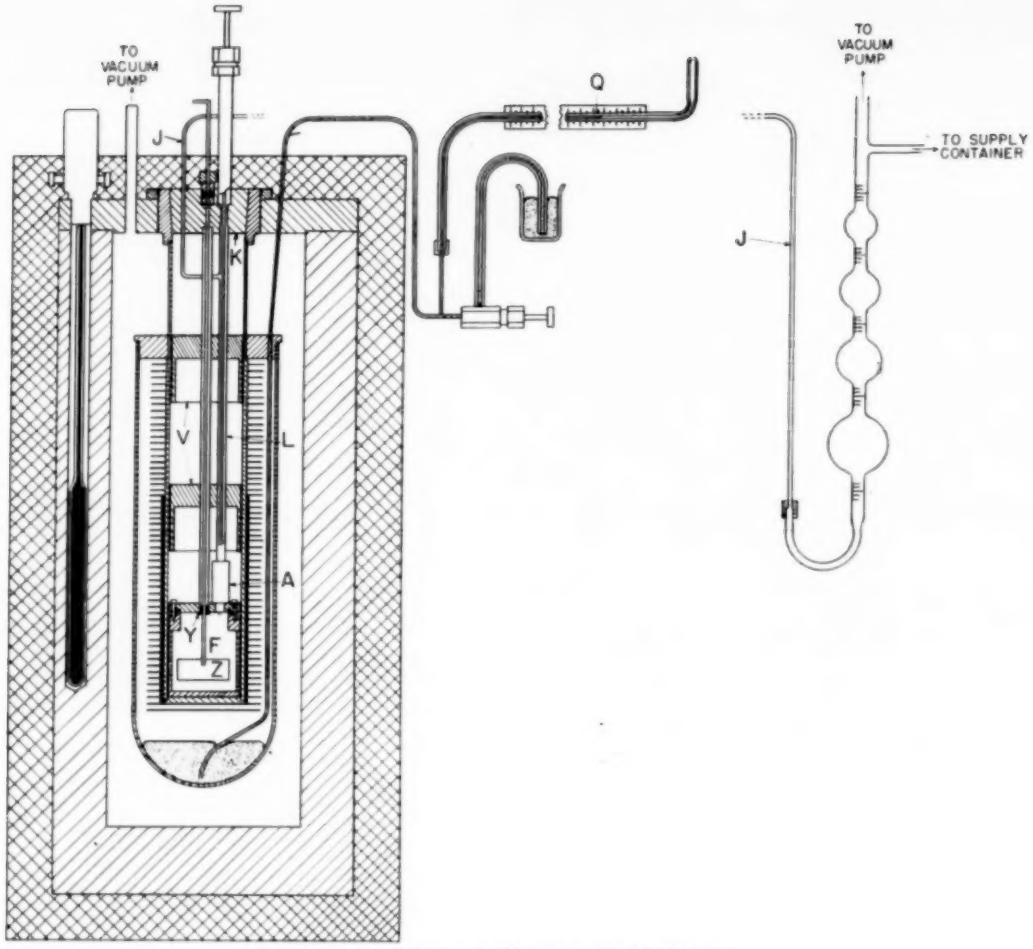

FIGURE 1. *Schematic diagram of calorimeter.*

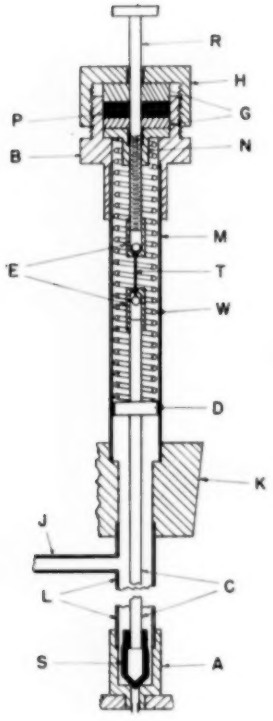

FIGURE 2. *Diagram of valve for admitting liquid to mixing vessel.*

glands G and Teflon packing P. The lower end of the spring presses against the shoulder D on the needle C. The rod R is threaded at its lower end where it passes through the threaded lower end of the nut N.

To the lower end of the rod R and the upper end of the needle C are hard soldered the sockets E. These were made by drilling axial holes of the diameter of R and C part way through short pieces of steel rod, and then drilling the rest of the way through the rods with a smaller drill. As shown in figure 2, the sockets E are connected by the tie rod T, at the ends of which are spheres of larger diameter than the small holes in the sockets. The valve is closed when the lower spherical end of the tie rod is low enough, as shown in figure 2, so that it hangs freely in the lower socket. The valve is opened by turning the rod R so as to raise it and the tie rod T until the valve needle is lifted off of its seat.

The characteristic features of the valve A which make it especially suitable for the present application are: (1) The energy introduced into the calorimeter in opening and closing the valve is small because the point does not rotate; and (2) this energy is uniform because of the constant closing pressure exerted by the spring. This valve effectively seals the opening into the mixing chamber. No thermal effect of

repeatedly opening and closing the valve was detected in blank experiments.

In measurements of heat of mixing the tubes J, L, and M (figs. 1 and 2) are completely filled with liquid, and each time the valve A is closed the rod R (fig. 2) is brought to the same position so that the volume of liquid in these tubes is always the same when the buret is read. There was no appreciable change in temperature of this liquid between the time of reading the buret before and after introducing liquid into the mixing chamber.

3.2. Experimental Method

The method of measurement consists essentially in adding a measured volume of solvent to a known mass of polymer (or polymer-solvent mixture) in the mixing chamber in the calorimeter, and observing the resulting thermal effect as indicated by the change in position of the mercury meniscus in the graduated capillary Q (fig. 1). Because it was not feasible to stir the mixture, which was very viscous in the composition range covered, the polymer sample was placed in the mixing chamber in such a manner as to promote rapid attainment of equilibrium between polymer and solvent. The sponge-like polymer was cut into fairly thin sheets which were separated in the mixing chamber by metal gauze, so that solvent vapor could circulate freely between the polymer sheets. As indicated in section 3.1, solvent came in contact with the polymer (or mixture) only as vapor. Experience in measurements of vapor pressure in this system [1] indicated that the approach to equilibrium under the conditions existing in the mixing chamber should be sufficiently rapid to permit reasonably accurate calorimetric measurements of heat of mixing. This is confirmed by the actual results of the calorimetric measurements, which indicated that equilibrium was attained in time intervals ranging from 30 min in mixtures of low benzene content to 90 min for mixtures containing approximately 50 percent benzene.

The procedure for making measurements of heat of mixing is as follows: The mixing chamber unit is removed from the calorimeter and a mantle of solid diphenyl ether is frozen around the outside of the central well as described previously [2].

The mixing chamber, detached from the remainder of the unit, is weighed first with only the metal gauze in it, and again after introducing about 1 g of polybutadiene. The mixing chamber is then attached to the remainder of the unit and connected through the tubes L and J, by means of the union in J, to a vacuum system. Solvent and permanent gases are removed from the polymer by prolonged evacuation to a pressure of less than 10^{-4} mm while heating to temperatures increasing gradually to a maximum of about 95° C. During this process most of the phenyl-beta-napthylamine used as an antioxidant sublimes from the sample. The valve A is then closed, and the mixing-chamber unit is replaced in the calorimeter and connected through the system of tubing described in section 3.1 to the buret (fig. 1). The observed mass of the sample was corrected for loss of phenyl-beta-naphthylamine and dissolved gases.

A supply of the solvent is placed in a container consisting of a glass bulb to which a brass valve is attached, and the container is connected through the valve to a vacuum pump. Air is removed from the liquid by freezing it in liquid air and evacuating the container, and by removal of part of the liquid by evacuation at room temperature. This procedure is repeated a number of times until, with the vacuum pump shut off, the pressure in the system after freezing the liquid is of the order of 10^{-5} mm of mercury. The valve on the container is then closed, the container disconnected from the vacuum system, inverted, and attached to the buret (fig. 1).

The buret and connecting tubing up to valve A (figs. 1 and 2), are evacuated until the pressure is reduced to less than 10^{-5} mm of mercury. The vacuum pump is then shut off and the valve on the supply container is opened, allowing the liquid to flow into the buret. The container is then disconnected from the buret, permitting air to flow into the buret above the liquid surface, the line to the vacuum pump is broken, and additional liquid introduced into the buret to bring the meniscus up to the zero graduation mark. It is believed that this procedure effectively eliminates the possibility of gas bubbles in the line between the buret and the mixing chamber, or in the tube M (fig. 2).

Before making a calorimetric measurement the jacket thermostat is adjusted so as to bring the temperature of the jacket within 0.001 deg C of that of the calorimeter. After allowing a reasonable time for the system to come to a steady state, readings are made at 10-min intervals of (1) the difference in temperature between calorimeter and jacket to about 0.0001 deg, (2) room temperature to the nearest 0.1 deg, and (3) the position of the mercury meniscus in the graduated capillary Q (fig. 1) to the nearest 0.1 mm (0.04 j or 0.01 cal). These measurements are continued for a sufficient length of time (30 to 60 min) to insure that the capillary reading is constant or changing at a uniform rate. The valve A (figs. 1 and 2) is then opened and liquid permitted to flow from the buret into the mixing vessel. The valve is closed again when the desired amount of liquid has been introduced into the mixing chamber, as indicated by the change in reading of the buret. The readings (1), (2), and (3) above are continued at 10-min intervals until the capillary reading has been constant or changing at a uniform rate for 30 to 50 min. The same procedure is followed in subsequent experiments, the final "rating period" of each experiment being taken as the initial rating period of the next. The volumes of liquid added in successive experiments were approximately 0.1, 0.1, 0.2, 0.4, and 0.3 cm^3. These volumes were measured at approximately 25.5° C. and were reduced to the corresponding volumes at 26.9° C.

3.3. Calculation of Results

The observed change in reading of the capillary in each experiment is multiplied by the calibration factor, 4.145 j/cm [2], to give the observed thermal effect. This is corrected for: (1) Thermal leakage determined from the rate of change of capillary reading in the rating periods preceding and following the "mixing period" in each experiment, (2) the work done by the atmosphere in forcing the liquid through the valve A into the evacuated mixing chamber, (3) the change in internal energy of the liquid introduced in each experiment in going from the buret at atmospheric pressure to nearly zero pressure in the mixing vessel, and (4) the change in energy of the vapor in the mixing vessel due to the difference between the vapor volumes and vapor densities at the beginning and end of the experiment. The correction (1) for thermal leakage ranged from zero to about 10 percent of the heat measured in a given experiment. The corrections (2) and (3) amount, respectively, to approximately -0.10 and $+0.04$ j/cm^3 of liquid added. Correction (4) was calculated from the known vapor volumes at the beginning and end of the experiment, the vapor densities as determined from the activity-composition relation for this system [1], and the energy of vaporization of benzene. The magnitude of this correction ranged from 8 to 20 percent of the heat measured.

The result of an experiment calculated as described above is, strictly speaking, the intrinsic energy of mixing at nearly constant pressure. This is practically equal to the heat (or enthalpy) of mixing at constant pressure, and is so designated in this paper.

4. Results

The observed values of heat of mixing are compared in table 1 with values calculated from the equation [2]

$$\Delta H^M = 12.00\ v_1 v_2, \qquad (1)$$

where ΔH^M is heat of mixing in joules per cm^3 of mixture, and v_1 and v_2 are volume fractions of solvent and polymer, respectively. The maximum difference between observed and calculated values corresponds to about 0.23 j (0.06 cal) in a calorimetric measurement. This is somewhat greater than the maximum deviation from the mean (0.15 j or 0.04 cal) in the calibration experiments [2], but larger calorimetric errors are to be expected in the present measurements because of the longer time required to reach equilibrium.[3]

[2] Equation (1) is of the same form as the well-known van Laar equation, but the constant factor 12.0 was determined empirically from the data. The solubility parameters [9] for benzene and polybutadiene yield the value 2.0 for this constant factor.

[3] Better agreement between observed and calculated values could be obtained by using an equation of the form $\Delta H^M = A v_1 v_2 (1 + B v_1)$, but it is not believed that the data are sufficiently accurate to justify this refinement.

In table 2 are given values of partial molal heat of dilution ($\Delta\overline{H}_1$) derived from eq (1); partial molal Gibbs free of energy of dilution ($\Delta\overline{G}_1$), derived from the relation $\Delta\overline{G}_1 = RT \ln a_1$, with

$$\ln a_1 = \ln v_1 + v_2 + 0.27 v_2^2 + 0.06 v_2^3; \qquad (2)$$

and partial molal entropy of dilution ($\Delta\overline{S}_1$) calculated from the relation

$$\Delta\overline{S}_1 = (\Delta\overline{H}_1 - \Delta\overline{G}_1)/T.$$

Equation (2) above is eq (2) for the activity of the solvent in reference [1].

TABLE 1. *Observed values of heat of mixing at 26.9°C compared with values calculated from eq (1)*

Volume fraction benzene, v_1	Heat of mixing, j/ml of mixture		
	Observed	Calculated	O−C
0.1088	0.986	1.164	−0.178
.1668	1.633	1.668	−.035
.2756	2.407	2.397	+.010
.4146	2.890	2.913	−.023
.4904	3.096	3.000	+.096

TABLE 2. *Values of partial molal enthalpy, Gibbs free energy and entropy of dilution at 26.9°C*

Volume fraction polymer v_2	$\Delta\overline{H}_1$	$\Delta\overline{G}_1$	$T\Delta\overline{S}_1$	$\Delta\overline{S}_1$
	j/mole	*j/mole*	*j/mole*	*j/mole deg*
0.5	269	−295	564	1.88
.6	387	−514	901	3.00
.7	527	−876	1,403	4.68
.8	689	−1,512	2,201	7.34
.9	871	−2,844	3,715	12.38
1.0	1,076	$-\infty$	∞	∞

Values of $\Delta\overline{S}_1/Rv_2^2$ are plotted versus v_2 in figure 3, where curve 1 represents the data of table 2, curve 2 represents similar results for the system natural rubber-benzene [5], and curve 3 represents values of $\Delta\overline{S}_1^*/Rv_2^2$, where $\Delta\overline{S}_1^*$ is the "configurational entropy" of dilution [6] calculated from the equation

$$\Delta\overline{S}_1^* = -R\,[\ln v_1 + v_2]. \qquad (3)$$

The curve 1 in figure 3 for the system polybutadiene-benzene is of the same general form as curve 3, but lies considerably above it. It is also higher than curve 2 for the rubber-benzene system [5], and than curves [6, p. 518] for the polymer-solvent systems polydimethylsiloxane (M=2850)–benzene [7], polystyrene-toluene, and polystyrene-butanone [8], all three of which lie below curve 3 (fig. 3) by varying amounts.

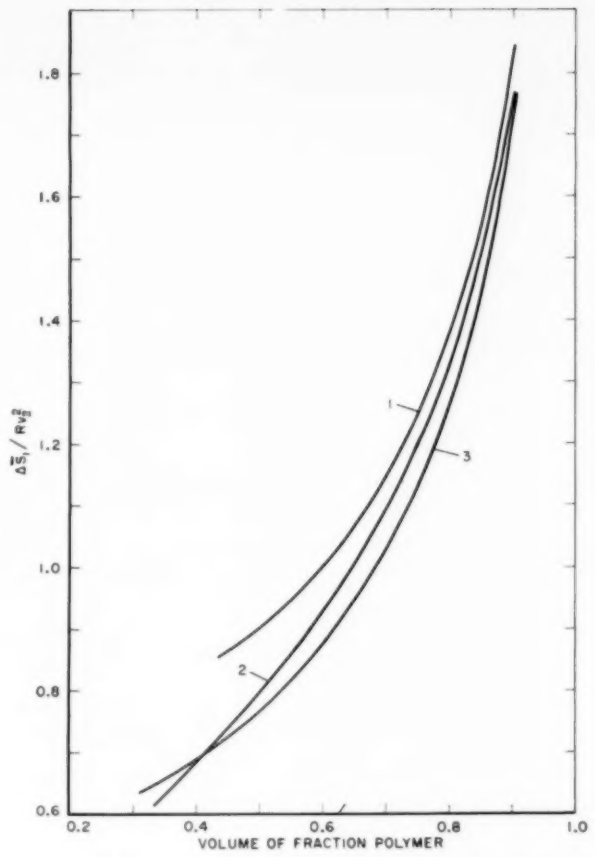

FIGURE 3. *Comparison of observed entropy of dilution* $\Delta\bar{S}_1$ *in the system polybutadiene-benzene (curve 1) with that for natural rubber-benzene (curve 2) and with* $\Delta\bar{S}_1^*$ *calculated from eq (3).*

5. References

[1] R. S. Jessup, J. Research NBS **60,** 47 (1958) RP2820.
[2] R. S. Jessup, J. Research NBS **55,** 317 (1955) RP2636.
[3] Selected values of properties of hydrocarbons, Table 5a Am. Petrol. Inst. Research Project 44, Carnegie Inst. of Technol. (1956).
[4] F. W. Schwab and E. Wichers, J. Research NBS **25,** 747 (1940) RP1357.
[5] G. Gee and W. J. C. Orr, Trans. Faraday Soc. **42,** 507 (1946).
[6] P. J. Flory, Principles of polymer chemistry, p. 512 (Cornell University Press, Ithaca, N. Y., 1953).
[7] M. J. Newing, Trans. Faraday Soc. **46,** 613 (1950).
[8] C. E. H. Bawn, R. F. J. Freeman, and A. R. Kamalidden, Trans. Faraday Soc. **46,** 677 (1950).
[9] J. H. Hildebrand and R. L. Scott, The solubility of nonelectrolytes, p. 387 (Reinhold Publishing Corporation, New York, N. Y., 1950).

WASHINGTON, July 23, 1958.

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Inrared High-Resolution Grating Spectrometer

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An infrared grating spectrometer which can be used as a single- or double-pass instrument has been built and set in operation. The collimating mirror has a focal length of 235 centimeters and the instrument has the highest resolution from 1,600 to 3,500 cm^{-1}. In order to have flexibility in scanning the spectra at different speeds, a special drive mechanism has been built which is made of spur gears and worm gears. The speeds range from 2.5 to 200 minutes of time per degree of rotation. Examples of the spectra resolved by the instrument are given. Lines separated by 0.05 cm^{-1} are completely resolved and two lines separated by 0.025 cm^{-1} are partially resolved.

1. Introduction

In recent years, cooled lead sulfide detectors have been made of high signal to noise ratio. By the use of these cooled PbS cells, much smaller slits can be used on the spectrometer and the diffracting grating may be the limiting factor in the resolution of the instrument. By double passing the radiation on a high-grade grating, a resolution approaching the theoretical resolving power has been obtained by Rank and his coworkers [1] in the region of 5,000 cm^{-1}. The instrument that is described in the present work is best suited for measurements in the region from 1,600 to 3,500 cm^{-1}, and partial resolution of 0.025 cm^{-1} has been obtained in this region.

2. Description of Instrument

A spectrometer has been designed which can be used as a single- or double-pass instrument. Two optical systems have been used for double passing the grating. One arrangement of the optical components is shown in figure 1. After the radiation has passed through the entrance slit it falls on an on-axis paraboloidal mirror (focal length 235 cm) and is rendered parallel. The mirror has a diameter of 16 in., and by using 7 in. on one side of the center it is effectively equal to a 3° off-axis system. From the grating, the parallel beam is intercepted by the optical flat and is reflected back to the grating where the beam almost retraces the incident path and falls on the second slit. The single-pass diffraction beam also falls on the second slit but its wavelength is slightly different from that of double-pass radiation. For the optical arrangement of figure 1, the dispersion is almost equal in the single- and double-pass spectra and is different only due to the inequality of the angle of the incident and reflected rays; and the wavelength regions are so close together that they cannot be separated by the transmission filters. In order to separate the two spectra, the optical flat is tilted a few minutes of arc from the vertical so that the two spectra are focused on the second slit with one above the other. The exit slit is then masked so that only the double-pass spectrum reaches the detector. When the instrument is used single pass, the optical flat is screened and the mask on the second slit is removed. The receiving surface of the lead sulfide cell is 2.5 by 0.2 mm and the radiation on 18 mm of the height of the slit is detected by the use of an ellipsoidal mirror giving a 7 to 1 reduction of image size.

[1] J. N. Shearer, T. A. Wiggins, A. H. Guenther, and D. H. Rank, J. Chem. Phys. **25,** 924 (1956).

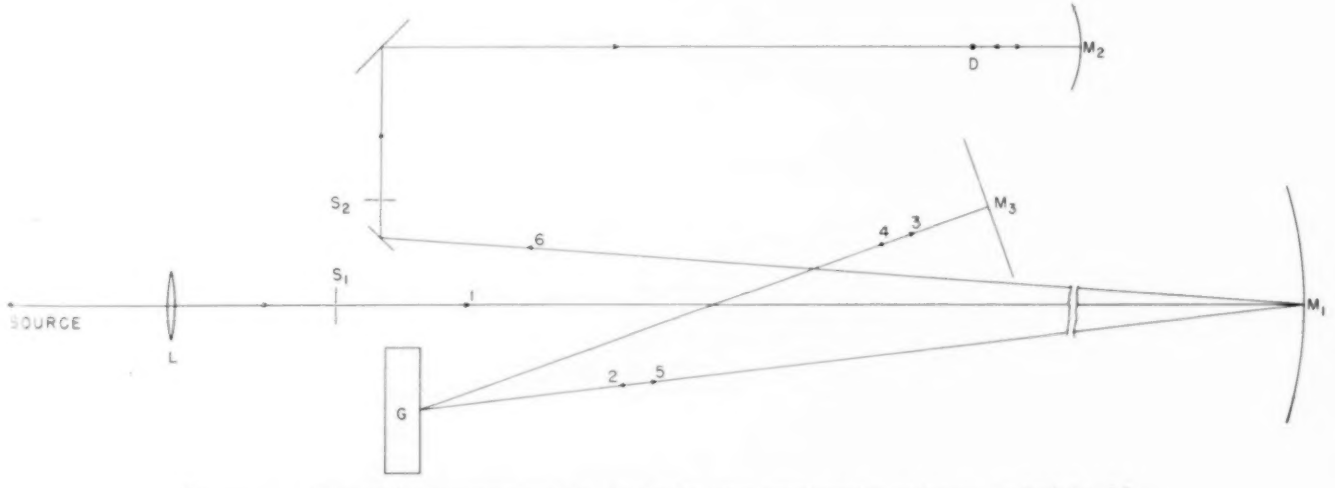

FIGURE 1. *The optical arrangement for the double-pass spectrometer using an optical flat* M_3.

M_1 is a paraboloidal mirror of 225 cm^{-1}, and M_2 is an ellipsoidal mirror with foci of 15 and 105 cm^{-1}.

The second optical system for double passing the radiation is shown in figure 2. The essential part of this system is the two small plane mirrors behind the entrance slit which send the energy back to the grating the second time. In order to remove the single-pass radiation, the beam is chopped in front of one of the small 45° mirrors. In this system the dispersion is, for all practical purposes, identical to its single-pass dispersion as the angle of the incident and reflected radiation are practically equal. The image on the second slit for single pass is curved. The two mirrors reverse the image and its curvature so that the double-pass image on the second slit is approximately straight.

In addition to the optical parts of the spectrometer, a number of auxiliary components are used. These consist of sources, filters, absorption cells, Fabry-Perot interferometers, PbS and PbTe photodetecting cells, amplifiers, and recorder. From 1 to 3.6 μ, a 300-w Sylvania enclosed zirconium arc is used for the source, and from 3.6 to 6 μ, a Nernst glower is used. In order to remove the higher order spectrum, transmission filters are set into the path of the radiant energy in front of the entrance slit of the spectrometer. A silicon filter is used from 1.2 to 2 μ, a germanium filter from 2 to 3.5 μ, and transmission filters made by Baird-Atomic from 3.5 to 6 μ. The filters transmit about 90 percent of the energy and are used instead of a foreprism arrangement. The absorption cell is 1 m in length and with the use of mirrors a 6-m path is obtained. Fluorite windows are used and the transmission of the cell for the 6-m path length is about 75 percent.

The spectrum is recorded on a two-pen recorder. One pen is used for the interferometer fringe system and the other pen records the absorption spectrum. The method of measuring the spectra from the charts has been described previously.[2] A disk chopper is used to modulate the radiation at 90 cps. The radiation falling on the cooled PbS cell is amplified by a 90-cps Wilson narrow-band-pass type amplifier[3] of low noise level. The spectrum is scanned by rotating the grating and for the highest resolution slow speeds are required. For example, in the region of 3,020 cm^{-1}, about 30 min of time is required to scan one wavenumber for the best formation of the lines. In order to adequately survey different regions of the spectrum under different levels of resolution a versatile drive system is desirable. A large number of speeds are possible by use of a gear box between the motor and the worm gear attached to the grating mount. A synchronous motor of 900, 1,800, and 3,600 rpm of about 1/30 hp is attached to a 10-to-1 reduction gear, which drives a four-speed gear box with reductions of 1 to 4, 1 to 1, 3 to 1, and 5 to 1. The gear box is reduced by a 60-to-1 precision worm, which then drives a pair of precision worms on the grating turn table which have reductions of 120 to 1, and 180 to 1. This arrangement of gears makes it possible to rotate the grating mount at 12 different speeds, the fastest speed being 2.5 min of time per degree of rotation and the slowest being 200 min/deg. Additional speeds which are faster and slower than those described above, can be obtained by changing the gears in the first reducer.

The uniformity of rotation of the system has been checked by the regularity of interference fringes of about 0.3-cm^{-1} spacing. The variation of the distance between successive fringes is less than 4 percent, which indicates that the irregularities of the drive do not introduce errors in measurement greater than 0.006 cm^{-1}. For rapid scanning or for moving from one spectral region to another, an auxiliary motor of 1,800 rpm can be automatically coupled directly to the output of the transmission gear box, which provides a rotational speed of 1° per half minute of time.

[2] Earle K. Plyler, L. R. Blaine, and E. D. Tidwell, J. Research NBS 55, 279 (1955) RP2630.

[3] R. C. Nelson and W. R. Wilson, Proc. Nat. Elec. Conf. 3 (1947).

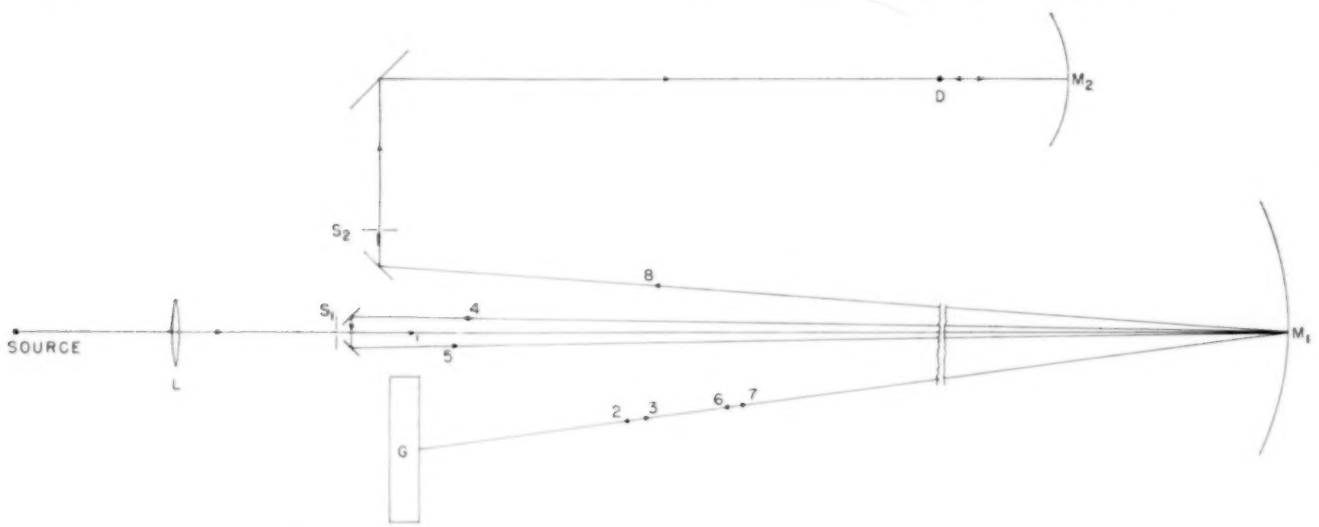

FIGURE 2. *The optical system for double pass using two small mirrors behind the entrance slit.*

The other mirrors are the same as those represented in figure 1.

3. Examples of Spectra Measured

The spectrometer has been in operation for about a year and some bands of several molecules such as methane, ethylene, ethane, ammonia, and cyclopropane have been measured. The classification of these spectra and the calculation of the molecular constants are now being made and the results will be given in other publications.

Some examples of the high resolution obtained by the instrument are given of parts of bands observed with slow scanning speeds. Figure 3 shows the P13 lines of methane as observed with a 10,000 lines/in. Bausch and Lomb grating using the optical system represented in figure 1. The pressure used was 0.1 mm (Hg) and the path length was 6 m. As the resolution of the instrument is increased, lower pressures of the gas can be used. When the P–13 transition of methane was measured on a single-pass spectrometer the last three lines were not so well separated and for the same maxima of absorption about 1 mm (Hg) pressure was necessary. The last two lines are separated by 0.055 cm^{-1} and the line widths at half intensity are about 0.023 cm^{-1}.

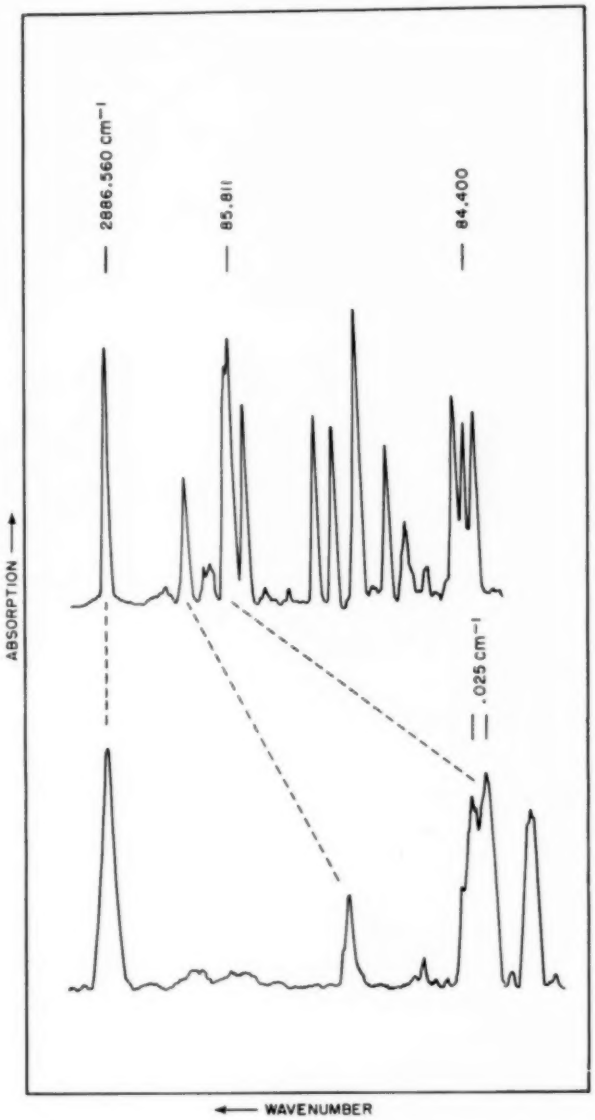

FIGURE 3. *The fine structure of the P13 line of the ν_3 band of methane.*

The lower curve is a part of the P13 line of methane scanned at the slowest rate of the drive. The two partially resolved lines are separated by 0.025 cm^{-1}. The pressure was 0.1 mm (Hg) and the path length 6 m. A grating with 10,000 lines/in. was used.

The lower part of the figure shows a slower scan (one-third speed) of several lines of the upper spectrum. The separation of the two partially resolved lines is 0.025 cm^{-1}. It is believed that the optical system is capable of still higher resolution, but until the noise of the electronics and the detector is reduced, the limit of resolution of the gratings and the optics cannot be determined.

An example of pressure broadening is shown in figure 4. Part of the ν_3 band of ammonia at 3,500 cm^{-1} overlaps the atmospheric absorption lines of water vapor. The width of the water vapor lines is about 0.15 cm^{-1} and the observed width of the ammonia lines at 2-mm pressure (Hg) is 0.03 cm^{-1}. On account of the large difference in line widths of the two substances it is easy to identify the two spectra. The spectra shown in figure 4 were observed with a Babcock 15,000 lines/in. grating which had a total of 120,000 lines.

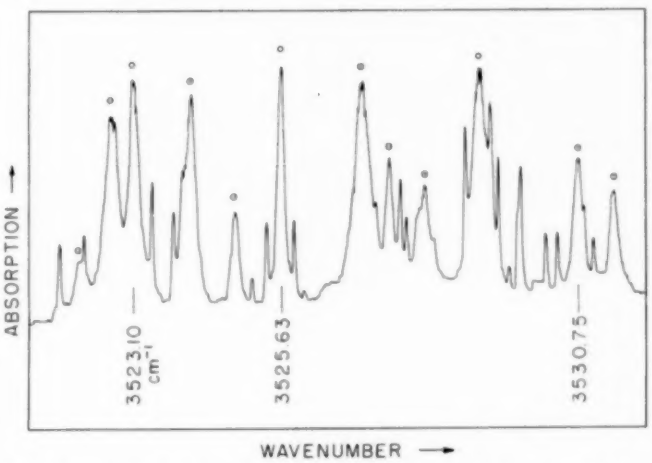

FIGURE 4. *The absorption spectrum of ammonia 2 mm* (Hg) *pressure, in the region of* 3,500 cm^{-1}.

The broad lines, marked with a circle over them, are produced by the atmospheric absorption of water vapor.

The actual limit of resolution of the instrument at the present time under the best conditions appears to be about 0.02 cm^{-1}. Larger gratings or more sensitive detectors, or both, will be required to make a further improvement in resolution.

The authors are indebted to Horace Babcock for making available to them one of his 15,000 lines/in. gratings.

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Determination of Titanium, Zirconium, Niobium, and Tantalum in Steels: Separations by Anion-Exchange

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A procedure is described for the determination of titanium, zirconium, niobium, and tantalum in steel. These elements are concentrated by selective precipitation with cupferron from a hydrochloric acid solution of the sample, and then ignited to the oxides. The oxides are fused, and dissolved in a hydrochloric-hydrofluoric acid mixture. Three separate eluates, containing titanium and zirconium, niobium, and tantalum, result from elution with mixtures containing ammonium chloride, hydrochloric acid, and hydrofluoric acid from a column of Dowex-1 anion-exchange resin. Boric acid is added to the eluates to complex the hydrofluoric acid, and the elements are precipitated with cupferron. Titanium is determined by the hydrogen-peroxide method, and zirconium by the phosphate-gravimetric method. Niobium and tantalum are determined by the hydroquinone- and pyrogallol-photometric methods, or by weighing the oxides.

1. Introduction

The increased use in recent years of elements that form complexes with carbon and nitrogen in metallurgical alloys has presented some interesting problems to the analytical chemist. For example, the high-temperature and heat-resisting alloys used in rockets and jet engines contain various combinations of tungsten, molybdenum, titanium, zirconium, niobium, tantalum, and aluminum in addition to the major elements, nickel, cobalt, iron, and chromium. Even the usual grades of stabilized stainless steels are becoming complex alloys through the use of scrap in melting charges. Because of the complexity of these materials, spectrographic and X-ray methods are desirable for production control and acceptance testing. Adequate chemical procedures for the analysis of standards used in calibrating these instruments are especially needed.

The difficulties encountered in handling combinations of zirconium, titanium, niobium, and tantalum are well known [10, 19].[1] During the last few years it has been shown [1, 20] that combinations of titanium, niobium, and tantalum can be separated by selective elution from cellulose columns with methyl ethyl ketone in combination with hydrofluoric and hydrochloric acids or their ammonium salts. Several papers [2, 6, 14, 15, 16] have shown that useful separations in this group of elements can be made on anion-exchange resin columns, using mixtures of hydrochloric and hydrofluoric acids as elution reagents.

The method described here provides for the determination of titanium, zirconium, niobium, and tantalum in the range of a few thousandths of one percent to approximately one-half percent in steels. The procedure involves most of the separations required in determining larger percentages of these elements and illustrates the application of the ion-exchange technique to otherwise very difficult separations. Direct photometric methods for the determination of molybdenum [10, p. 315] and tungsten [18] in steels are available for this concentration range, and these elements are not considered except as they affect other determinations.

[1] Figures in brackets indicate the literature references at the end of this paper.

A concentration of titanium, zirconinum, niobium, and tantalum is effected by cupferron precipitation [4, 5] with most of the iron present in the reduced condition. The small amount of iron coprecipitated serves as a gathering agent. Most of the chromium, nickel, cobalt, manganese, and iron pass into the filtrate, so that a satisfactory concentration can often be made from a sample as large as 25 g.

The cupferron precipitate is ignited to the oxide, leached with hydrochloric acid, and filtered. The filtrate is evaporated nearly to dryness. The insoluble material is ignited, treated with sulfuric and hydrofluoric acids to eliminate silica, and fused in sodium pyrosulfate. A mixture containing 50 percent by volume of hydrochloric acid and 10 percent by volume of hydrofluoric acid is added to the evaporated filtrate, and the melt is dissolved in the resulting solution.

The solution is transferred to an anion-exchange column, and the titanium and zirconium are eluted with a 50-percent hydrochloric 10-percent hydrofluoric acid solution. A second fraction containing molybdenum, tin, and iron is eluted with a mixture containing 12.5 percent by volume of hydrochloric acid, 20 percent by volume of hydrofluoric acid and 7.2 percent by weight of ammonium chloride, and discarded. Niobium is collected in a third fraction by elution with an ammonium chloride-hydrofluoric acid solution. Tantalum is collected in a fourth fraction by elution with an ammonium chloride-ammonium fluoride solution adjusted to a pH of 5 to 6.

The first fraction containing the titanium and zirconium (and in addition, such elements as chromium, nickel, tungsten, and vanadium) is mixed with a boric acid solution to complex the hydrofluoric acid. A small amount of iron is added as a gatherer, and a precipitation is made with cupferron. The precipitate is ignited, fused in pyrosulfate and dissolved in hydrochloric acid. A sodium hydroxide precipitation [10, p. 579] is made to eliminate vanadium and tungsten, and the precipitate is ignited. The oxide mixture is fused in pyrosulfate and dissolved in diluted sulfuric acid. Titanium is determined in a suitable aliquot by a differential photometric measurement of the colored complex formed

with hydrogen peroxide [10, p. 581]. The solutions used for the photometric determination of titanium are combined, and zirconium is determined by the phosphate method [10, p. 569].

The third fraction containing the niobium is treated with boric acid to complex the hydrofluoric acid, and zirconium, low in niobium and titanium, is added as a coprecipitant. After precipitation with cupferron, the ignited oxide is fused in pyrosulfate and dissolved in ammonium oxalate solution. A suitable aliquot of the solution is evaporated to fumes with sulfuric and nitric acids to destroy the oxalate ion. The niobium is determined photometrically with hydroquinone [11, 12] in concentrated sulfuric acid. Larger amounts of niobium, such as are encountered in type 347 stainless steel, can be precipitated with cupferron after the addition of boric acid, ignited to the oxide, and weighed.

Tantalum in the fourth fraction is recovered from the eluate by precipitation with cupferron after the addition of boric acid and zirconium. The ignited oxide is fused in pyrosulfate and dissolved in ammonium oxalate-ammonium citrate solution. The photometric determination of tantalum employs the color reaction with pyrogallol [10, p. 610]. Larger amounts of tantalum can be precipitated with cupferron after the addition of boric acid, ignited to the oxide and weighed.

The present procedure is somewhat long, as two days are required to carry out the ion-exchange separations, unless the columns are operated continuously, and several days are required to finish the various determinations. The method does, however, compare favorably in time and ease of operation with the other chemical methods available for this combination of elements, and lends itself readily to handling a number of samples at the same time if enough columns are prepared.

2. Apparatus and Resins

Ion-Exchange Columns. The columns are constructed of polystyrene and are approximately 12 in. long and of 1 in. inside diameter. A simple column can be prepared from a 12-in. length of polystyrene tubing as follows: The bottom of the tube is closed by a waxed No. 5 rubber stopper with a 3/16-in. hole. A 6-in. length of polystyrene tubing, 3/16 in. outside diameter, 1/16-in. bore, is inserted into the hole flush with the upper surface of the stopper. Another 6-in. length of this tubing is attached to the smaller tube with a 2-in. length of Tygon R tubing, and the flow controlled by a hosecock clamp on the Tygon tubing. However, if a number of analyses are to be made, it is convenient to arrange the columns so that a number can be operated with a minimum of attention, as has been done previously with glass columns [7]. Plastic columns suitable for such an assembly have been developed [13]. The columns used in this work were obtained and assembled as illustrated in figure 1.

These columns are equipped with machined "Dole-type" fittings of polystyrene. Inlet and outlet tubes are of polyethylene; flexible connections where necessary are made of Tygon R tubing. The flow of solutions is controlled by hosecock clamps on the flexible connections. The connections should be carefully done and checked to avoid any possibility of leakage of the solutions containing hydrofluoric acid.

Resins. Dowex-1, 200- to 400-mesh, 8- to 10-percent divinylbenzene cross linkage are used. Experience over a period of several years has shown that the mesh size of these resins may vary considerably from lot to lot. In order to avoid difficulty, the resins as received are air dried, and sieved through a 270-mesh sieve. Material retained on the 270-mesh sieve is used for other purposes. Most of the fines are removed from the fraction passing the 270-mesh sieve as follows: Prepare a suspension of the resin in diluted hydrochloric acid (1+19). This terminology denotes 1 volume of concentrated hydrochloric acid, sp gr 1.18, diluted with 19 volumes of water. If no dilution is specified, the concentrated analytical reagent is meant. The coarser fraction is allowed to settle 10 to 15 min, and the fines removed by decantation. Repeat the process several times until most of the very fine material has been removed from the suspension.

Cover the bottom of the ion-exchange column with a layer of acid-resistant vinyl-chloride plastic wool, 1/4- to 3/8-in. thick. Add portions of the resin suspension to obtain a settled column of the resin 6 to 7 in. high. The loaded column should be run through several cycles of elution with alternate additions of diluted hydrochloric acid (3+1) and diluted hydrochloric acid (1+9) to remove the remainder of the fines. The column is then washed with diluted hydrochloric acid (1+3) and is ready for use. Resin columns prepared in this way have been used for several years. The only maintenance required is to empty and refill the column with the resin charge if the flow rate becomes excessively slow due to packing. The resin charge should not be allowed to become dry.

Polyethylene Ware. 250-ml and 600-ml Griffin-form beakers are required. The high-temperature polyethylene ware is useful for evaporations at steam-bath temperatures. Bottles are used for preparing and dispensing acid mixtures containing hydrofluoric acid.

Colorimeter. An Evelyn type of colorimeter, including filters, voltage stabilizer, and galvanometer, was used for the measurements reported. Matched test tubes (22 by 175 mm) were used as absorption cells.

3. Procedures and Discussion

3.1. Preparation of the Solution for Ion-Exchange Separations

Reagents

Cupferron Solution (60 g/liter). Dissolve 6 g of cupferron in 90 ml of water, dilute to 100 ml, and filter through a dry filter. This solution should be prepared as needed and cooled (5° C), as the solution is not stable.

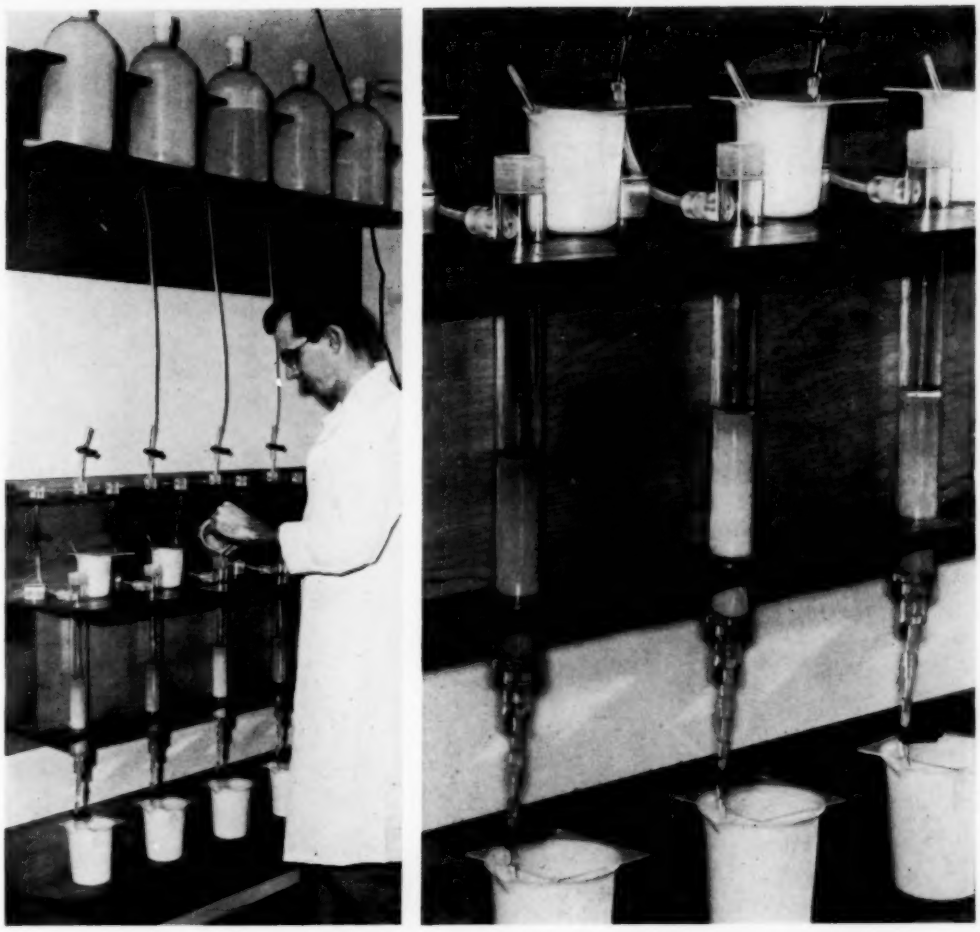

FIGURE 1. *Assembly (left) and close-up view (right) of ion-exchange columns.*

Cupferron Wash Solution. Add 25 ml of cupferron solution to 975 ml of cold (5° C) diluted hydrochloric acid (1+9). Prepare as needed.

Procedure

Transfer 5 to 25 g of the sample to a covered 600- or 800-ml beaker, and add 225 to 450 ml of diluted hydrochloric acid (1+2). Warm the solution on a steam bath, or if necessary over a burner, until the sample dissolves. Adjust the volume of the solution with water to 400 to 500 ml, so that the solution contains approximately 15 percent by volume of hydrochloric acid. (One gram of iron requires approximately 3 ml of hydrochloric acid for solution.)

Cool the solution to 5° C, and add cupferron solution dropwise and with continuous stirring until the iron starts to precipitate. The precipitate will begin to coagulate when precipitation of titanium, zirconium, niobium, tantalum, vanadium, etc., is complete. Add several milliliters of cupferron in excess (approximately 25 to 30 ml in total), which will cause the precipitate to assume a reddish color. The precipitated iron will act as a "gatherer" for the other elements. Add a ball of paper pulp equivalent to about one-half of an 11-cm filter paper, stir until the pulp is well dispersed, and allow the precipitate to settle. Filter through a double 7-cm close-texture filter paper fitted to a Büchner funnel and precoated with some filter pulp. Transfer the precipitate to the funnel and wash well, using 400 ml of cupferron wash solution. Transfer the precipitate and papers to a 30-ml porcelain crucible, and carefully ignite at a low temperature (500° to 550° C) until carbon is removed.

Transfer most of the ignited oxides to a 250-ml beaker, and dissolve the remainder in the crucible in warm diluted hydrochloric acid (1+1). Finally police and wash the crucible, with the same acid, transferring the washings to the 250-ml beaker. Adjust the volume to about 30 to 35 ml with diluted hydrochoric acid (1+1), and digest on the steam bath for several hours. Add paper pulp, and filter the warm solution through a 9-cm close-texture paper containing pulp, catching the filtrate in a 250-ml high-temperature polyethylene beaker. Transfer the undissolved residue to the paper and wash with diluted hydrochloric acid (1+1). Evaporate the filtrate and washings to a volume of approximately 5-ml, and reserve. Transfer the precipitate and paper to a 25-ml platinum crucible, and ignite at a low temperature.

Add 1 ml of sulfuric acid and 10 to 15 ml of hydrofluoric acid to the crucible, and remove the hydro-

fluoric and sulfuric acids by heating on an air or sand bath, being careful that the sulfuric acid does not creep over the top of the crucible. Finally ignite at a low temperature, and fuse the oxides with 1 g of sodium pyrosulfate.

Add 30 ml of a hydrochloric-hydrofluoric acid mixture, containing 50 percent by volume of hydrochloric acid and 10 percent by volume of hydrofluoric acid, to the polyethylene beaker. Transfer the crucible and melt to the beaker, and warm on a steam bath. Manipulate the crucible with a polyethylene stirring rod until the melt dissolves, remove the crucible with the rod or platinum-tipped tongs, and wash well with the 50-percent hydrochloric-10-percent hydrofluoric acid solution. The solution should be clear for the separations which follow to succeed, and the volume should be approximately 50 to 75 ml.

If large quantities (25 mg or more) of titanium or zirconium are present, the amount of flux and the volume may have to be increased to obtain a clear solution. Alternatively, the solution may be filtered through a close-texture paper onto the column, and the paper washed thoroughly with the hydrochloric-hydrofluoric acid solution to dissolve any insoluble material.

The fusion is made with sodium pyrosulfate because the potassium salt forms insoluble fluoroborates in the procedure described in section 3.3.a. If titanium and zirconium determinations are not desired the fusion may be made with potassium pyrosulfate, provided the tantalum does not exceed 50 mg or so; otherwise sparingly soluble potassium fluorotantalate will precipitate. Such solubility considerations do not arise with mixtures of hydrous oxides or metals, which can be dissolved directly in the mixed acids.

3.2. Ion-Exchange Separation of Titanium and Zirconium (+Hafnium), Niobium, and Tantalum

Reagents

Hydrochloric-Hydrofluoric Acid Solution. Add 500 ml of hydrochloric acid to 300 ml of water, add 100 ml of hydrofluoric acid, dilute to 1 liter with water, and mix well. The solution is referred to as 50–10 mixture in the procedure.

Ammonium Chloride Solution (240 g/liter). Dissolve 240 g of ammonium chloride in 800 ml of water by warming, and dilute to 1 liter with water. Filter to remove insoluble material. This solution is used as a stock solution in preparing the three solutions which follow.

Ammonium Chloride-Hydrochloric-Hydrofluoric Acid Solution. Transfer 300 ml of ammonium chloride solution, 200 ml of hydrofluoric acid and 125 ml of hydrochloric acid to a polyethylene bottle. Dilute to 1 liter with water, and mix well. This solution is referred to as 7–12 ½–20 mixture in the procedure.

Ammonium Chloride-Hydrofluoric Acid Solution. Transfer 600 ml of ammonium chloride solution and 40 ml of hydrofluoric acid to a polyethylene bottle, dilute to 1 liter with water, and mix well. This solution is referred to as 14–4 acid mixture in the procedure.

Ammonium Chloride-Ammonium Fluoride Solution. Transfer 600 ml of ammonium chloride solution and 40 ml of hydrofluoric acid to a polyethylene beaker. Adjust the solution to a *p*H of 5 to 6 with ammonium hydroxide (approximately 80 to 85 ml will be required), and dilute to 1 liter with water. This solution must be prepared with reasonable care, as a solution which is too acid will not completely elute the tantalum in the volume specified in the procedure. A solution which is too alkaline will precipitate tantalum in the column, spoiling the determination and the one which follows. This solution is referred to as 14–4 neutral mixture in the procedure.

Procedure

Transfer 50 ml of the 50–10 mixture to the column in small increments (5 to 10 ml), and drain the acid to 1 cm above the resin bed. Discard the eluate. Transfer the solution, prepared according to the directions in the previous section, in small increments (5 to 10 ml) to the column with the bottom hose-cock clamp open. Add the sample as the solution moves down the column until all the sample has been transferred. Wash the beaker 4 to 5 times with 5-ml portions of the 50–10 mixture, and finally wash down the sides of the column several times with the same mixture. Discard the first 20 or 25 ml of solution from the column, and collect the remainder of the first fraction, containing the titanium and zirconium (+hafnium) along with vanadium, tungsten, chromium, etc., in a 600-ml polyethylene beaker. Add a total of 350 ml of the 50–10 mixture, this volume to include the washings and the solution used to elute the fraction. The hose-cock clamp should be adjusted so that the flow of the solution is approximately 100 to 125 ml/hr. Allow the solution to drain to the top of the resin, and wash down the sides of the column with six or seven 5-ml portions (a total of about 35 ml) of the 7–12 ½–20 mixture, allowing the solution to drain to the top of the column each time. Reserve the beaker containing the first eluate, and replace it with another 600-ml polyethylene beaker.

Add a total of 350 ml of the 7–12 ½–20 mixture at a flow-rate of approximately 100 to 125 ml per hour, and allow the solution to drain to the top of the column. Wash the sides of the column with six or seven 5-ml portions of the 14–4 acid solution, remove the beaker containing the second fraction, and replace with another 600-ml polyethylene beaker. The second fraction contains primarily iron, and molybdenum and tin if present, and can be discarded.

Add a total of 300 ml of the 14–4 acid mixture, maintaining the technique and flow-rate described in the previous paragraph. Wash the sides of the column with approximately 25 to 30 ml of the 14–4 neutral mixture, remove the beaker containing the third fraction (niobium) and reserve. Replace the beaker with a 600-ml polyethylene beaker.

Elute the fourth and final fraction by the addition of a total of 300 ml of the 14–4 neutral mixture, and reserve the solution for the determination of tanta-

lum. The column is cleaned by the addition, in increments, of 50 ml of diluted hydrochloric acid (1+3), after which it is ready for the next sample.

It should be mentioned that painful burns can result from careless handling of hydrofluoric acid solutions. Any spills should be promptly washed up, and borax, or similar proprietary compounds, should be used several times a day in washing the hands or any skin area exposed to hydrofluoric acid.

3.3. Determination of Titanium, Zirconium (+Hafnium), Niobium, and Tantalum

a. Titanium

Reagents

Ferric Sulfate Solution (50 g/liter). Dissolve 5 g of hydrated ferric sulfate (low in titanium and zirconium) in 90 ml of diluted sulfuric acid (1+9), and dilute to 100 ml with diluted sulfuric acid (1+9).

Sodium Hydroxide Solution (100 g/liter). Dissolve 10 g of sodium hydroxide in 80 ml of water, and dilute to 100 ml.

Ammonium Nitrate Wash Solution (20 g/liter). Dissolve 10 g of ammonium nitrate in 400 ml of water, and dilute to 500 ml.

Standard Titanium Sulfate Solution (1 ml≈0.25 mg of titanium). Transfer 0.4170 g of titanium dioxide (a suitable portion of NBS Standard Sample 154a may be used) to a 250-ml Erlenmeyer flask, add 10 g of ammonium sulfate and 25 ml of sulfuric acid, insert a short-stemmed glass funnel in the neck of the flask and heat cautiously to incipient boiling while rotating the flask over a free flame. Continue the heating until complete solution has been effected and no unattacked material remains on the wall of the flask. Cool and rapidly pour the solution into 450 ml of cool water which is vigorously stirred. Rinse the flask with diluted sulfuric acid (5+95). Transfer the solution to a 1,000-ml volumetric flask, dilute to the mark with diluted sulfuric acid (5+95), and mix thoroughly.

Procedure

Transfer 40 g of boric acid to a 1,500-ml beaker, add 700 ml of water, and warm to dissolve the acid. Add the first fraction of solution containing the titanium and zirconium to the warm boric acid solution with continuous stirring, and add by pipet 2 ml of the ferric sulfate solution. Cool to 5° C, and add 25 to 30 ml of cupferron solution slowly while stirring. Add paper pulp, stir the solution well to distribute the pulp, and allow the precipitate to settle for 10 to 15 min. Filter through a double thickness of close-texture filter paper fitted to a 7-cm Büchner funnel and precoated with a little filter pulp. Transfer the precipitate to the funnel, and wash well with 400 ml of cold (5° C) cupferron wash solution. Transfer the paper and precipitate to a 25-ml porcelain crucible, and ignite at a low temperature until the carbon has burned. Fuse the ignited oxides in 1 to 2 g of potassium pyrosulfate, transfer the crucible to a 250-ml beaker, and dissolve the melt with 30 ml of diluted hydrochloric acid (1+9). Remove the crucible, and wash with warm water.

Add sodium hydroxide solution until the solution is neutral to litmus paper, then add an excess of 5 ml and heat to boiling. Boil for 5 min, add a small amount of paper pulp, and filter the warm solution through a close-texture paper containing pulp. Transfer the precipitate to the paper, and wash 12 to 15 times with ammonium nitrate (20 g/liter) wash solution. Transfer the paper and precipitate to a porcelain crucible, and ignite at a low temperature. Fuse the ignited oxides in 1 g of potassium pyrosulfate, dissolve the melt in 30 ml of diluted sulfuric acid (1+9), and add a little paper pulp. Filter the solution through a close-texture paper containing paper pulp, catching the filtrate in a 100-ml volumetric flask. Wash 8 to 10 times, and dilute to volume, with diluted sulfuric acid (1+9). If necessary, transfer a suitable aliquot containing not more than 2.5 mg of titanium to a 100-ml volumetric flask and dilute to the mark with diluted sulfuric acid (1+9). Since the solutions are to be combined for the determination of zirconium, all aliquoting, cell rinsing, etc., should be carried out in such a way as to achieve this objective.

For the photometric determination of titanium, rinse a photometer cell 3 times with 3 to 4 ml of the solution from the 100-ml volumetric flask, transferring the rinsings to a 400-ml beaker. Transfer 15 ml of the solution to a 2-cm photometer cell for use as a reference solution. Add 1.0 ml of hydrogen peroxide (30%) to the solution remaining in the flask and mix thoroughly. Transfer a suitable portion to the matched 2-cm photometer cell for use as the sample solution. Using the reference solution, adjust the photometer to the initial setting using a narrow light band centered at approximately 410 mμ. While maintaining this photometer adjustment, take the photometric reading of the sample solution.

Transfer the solutions to the 400-ml beaker, and reserve for the determination of zirconium. Determine the amount of titanium from a calibration curve prepared as follows: Transfer 0.0, 2.0, 5.0, and 10.0 ml of standard titanium solution to each of four 100-ml volumetric flasks, and dilute to volume with diluted sulfuric acid (1+9). Continue as described in the preceding paragraph, and plot the photometric readings of the calibration solutions with respect to milligrams of titanium, or calculate a factor [8]. The solutions obey Beer's Law and blanks are usually negligible. Since "difference" photometric measurements of this type are dependent for accuracy on an additive absorbancy function, a narrow-band filter photometer or spectrophotometer is desirable for the measurements.

In preparing the solution for the sodium hydroxide separation, a turbid solution is obtained if the sample contains appreciable tungsten. The sodium hydroxide separation removes most of the tungsten, along with the vanadium. In order to check for the complete removal of vanadium, photometric readings on the peroxide treated solution were made at approximately 515 mμ. A change in ratio of the absorbancy at 410 mμ to that at 515 mμ will indicate

vanadium. Vanadium occlusion in the precipitate amounts to less than the equivalent of 0.1 mg of titanium, even where as much as 50 mg of vanadium is involved.

b. Zirconium (+Hafnium)

Reagents

Ammonium Phosphate Solution (300 g/liter). Dissolve 60 g of diammonium hydrogen phosphate in 150 ml of water. Filter if necessary, and dilute to 200 ml with water.

Ammonium Nitrate Wash Solution (50 g/liter). Dissolve 25 g of ammonium nitrate in 400 ml of water, and dilute to 500 ml with water.

Procedure

Transfer all of the sample solution and washings from the titanium determination to a 400-ml beaker, and adjust to a volume of 200 ml or less, with the acidity approximately 10 percent by volume in sulfuric acid. Add 1 to 2 ml of hydrogen peroxide (30%) and 25 ml of ammonium phosphate solution, and allow to stand overnight at a temperature of 35° to 40° C. (with a milligram or less of zirconium, let the solution stand a day or two). Add 1 ml of hydrogen peroxide, cool, add paper pulp, and filter through a close-texture paper containing a little pulp. Transfer the precipitate to the paper, and wash 18 to 20 times with ammonium-nitrate wash solution (50 g/liter). Unfortunately, the zirconium phosphate precipitate tends to change composition, so the washing technique should be such as to leave the proper composition [10, p. 569, footnote 20]. Transfer the paper and precipitate to a weighed porcelain crucible, and ignite first at a low temperature to remove carbon, and finally ignite at 1,050° C. for 20 min. Cool, and weigh as $ZrP_2O_7 + HfP_2O_7$.

The precipitate also contains any hafnium in the alloy, since the acid mixture chosen for elution does not give an appreciable fractionation of titanium, zirconium, and hafnium. If suitable conditions can be established without too much extra manipulation, the use of mandelic acid [9,17] as a precipitant is attractive, particularly for the larger amounts where the advantage of the phosphate conversion factor is more than outweighed by the lack of a definite composition. A good color reaction reasonably specific for zirconium is also needed for small quantities, where the normal hafnium ratio of 2 or 3 percent is not critical.

c. Niobium

Reagents

Zirconium Sulfate Solution (1 ml≏approximately 10 mg of zirconium). Dissolve 3.90 g of zirconium sulfate tetrahydrate in 75 ml of diluted sulfuric acid (1+19), transfer to a 100-ml volumetric flask, and dilute to volume with diluted sulfuric acid (1+19). This solution must be low in titanium and iron, as well as niobium and tantalum. It was prepared from salt purified by the method of Clabaugh and Gilchrist [3].

Ammonium Oxalate Solution (40 g/liter). Dissolve 40 g of ammonium oxalate in 900 ml of warm water, filter if necessary, and dilute to 1,000 ml with water.

Stannous Chloride Solution (200 g/liter). Dissolve 100 g of stannous chloride dihydrate in 400 ml of diluted hydrochloric acid (1+1) by heating on the steam bath. Cool and dilute to 500 ml with diluted hydrochloric acid (1+1).

Hydroquinone Solution (50 g/liter). Dissolve 20 g of hydroquinone in 400 ml of sulfuric acid.

Standard Niobium Solution (1 ml≏40 μg of niobium). Transfer 0.0115 g of niobium pentoxide to a porcelain crucible. Add 1 g of potassium pyrosulfate, heat to fuse the niobium oxide, and dissolve the cooled melt with continuous stirring in 30 ml of warm ammonium oxalate solution. Transfer the cooled solution to a 200-ml volumetric flask and dilute to volume with ammonium oxalate solution. This solution should be prepared as needed.

Procedure

To the third fraction (approximately 300 ml) containing the niobium, add 15 g of boric acid, 70 ml of hydrochloric acid, 80 ml of water, and 2 ml of zirconium sulfate solution. Warm on the steam bath (30° to 35° C) and stir occasionally to dissolve the boric acid. Cool to 5° C, and add slowly while stirring, 30 ml of cupferron solution. Add paper pulp, stir well to distribute the pulp and allow to stand 10 to 15 min. Filter through a double thickness of 7-cm close-texture paper fitted to a Büchner funnel. Transfer the precipitate to the filter, and wash well using 400 ml of cold cupferron wash solution. Transfer the paper and precipitate to a porcelain crucible and ignite at a low temperature (500° to 550° C). Add 1 g of potassium pyrosulfate to the crucible, and fuse to dissolve the mixed oxides. Transfer the crucible and melt to a 100-ml beaker and dissolve the melt in 25 ml of warm ammonium oxalate solution. The fusion should be agitated with a stirring rod while dissolving, in order to prevent a localized high concentration of niobium which might lead to the precipitation of the hydrous oxide. Transfer the solution to a 100- or 200-ml volumetric flask, and dilute to volume with ammonium oxalate solution. Transfer a suitable aliquot containing not more than 0.3 mg of niobium to a weighed 100-ml beaker.

Add 10 ml of diluted sulfuric acid (1+1), 5 ml of nitric acid, and 3 to 5 ml of hydrochloric acid. Heat on a hot plate until moderate fumes of sulfuric acid are evolved, cool, and wash down the sides of the beaker with water. Cool, add 2 or 3 drops of hydrogen peroxide (30%), and again heat to moderate fumes of sulfuric acid. Repeat the washing and hydrogen peroxide addition, and again evaporate to fumes. Finally, wash down the sides of the beaker, and heat to moderate fumes of sulfuric acid. Cool, add 1 drop of stannous chloride solution, and mix well by swirling the beaker. Add hydroquinone solution to make 100 g of solution in the beaker, and mix the solution thoroughly. Transfer a suitable portion of hydroquinone solution to a 2-cm photometer cell for use as a reference solution. Transfer a portion of the test solution prepared above to a

matched 2-cm photometer cell for use as the sample solution. Using the reference solution, adjust the photometer to the initial setting using a light band centered at 490 mμ. While maintaining this photometer adjustment, take the photometric reading of the sample solution.

Determine the amount of niobium present in the test solution from a calibration curve prepared as follows: Transfer 0.0, 2.0, 5.0, and 10.0 ml of standard niobium solution (40 μg/ml) to four weighed 100-ml beakers, and continue as directed in the preceding paragraph. Plot the photometric readings of the calibration solutions with respect to micrograms of niobium. The hydroquinone photometric method has an appreciable temperature coefficient (approximately 0.6 to 0.7 %/deg), so that the photometric readings must be carried out at a controlled temperature, or a separate set of calibration solutions must be carried along with each set of determinations. Since it was not convenient to control the temperature, the latter alternative was used for the determinations reported in this paper. The photometric measurements on these solutions follow Beer's Law, and blanks are usually negligible. The wavelength selected for the measurements is on the long wavelength side of the peak absorbancy primarily to extend the concentration range, and because somewhat better precision was obtained.

It is more convenient to determine niobium in a suitable aliquot by developing a color with hydrogen peroxide [21] in a sulfuric-phosphoric acid medium, but the zirconium used as a gatherer interferes in this procedure. Attempts to use tin as a gatherer were not successful because the ignited oxides do not fuse readily in pyrosulfate. If 20 mg or more of niobium is involved, the determination can be conveniently completed by precipitation with cupferron as described in the first paragraph of this procedure. The addition of zirconium sulfate solution is of course omitted, and the oxide ignited at 1,000° C and weighed as niobium pentoxide. Losses due to incomplete precipitation or solubility do not exceed 0.5 mg of niobium.

d. Tantalum

Reagents

Ammonium Oxalate-Ammonium Citrate Solution. Add 25 ml of sulfuric acid to 975 ml of water, and mix well. Add 40 g of ammonium oxalate monohydrate and 50 g of diammonium citrate, and warm (30° to 35° C) on the steam bath to dissolve the salts. Filter through a dry filter, if necessary, to obtain a clear solution.

Pyrogallic Acid Solution (200 g/liter). Dissolve 100 g of pyrogallic acid in 400 ml of ammonium oxalate-ammonium citrate solution, dilute to 500 ml with the same solution, and transfer to a glass-stoppered bottle. This solution is not especially stable, and a fresh solution should be prepared if the blank photometric reading is excessive. Occasional lots of pyrogallic acid have been observed to give a solution which is excessively colored, even though freshly prepared.

Standard Tantalum Solution (1 ml≅0.125 mg tantalum). Transfer 0.0305 g of tantalum pentoxide to a porcelain crucible. Add 1 g of potassium pyrosulfate to the crucible, heat to fuse the oxide, and dissolve the cooled melt with continuous stirring in 75 ml of warm ammonium oxalate-ammonium citrate solution. Transfer the cooled solution to a 200-ml volumetric flask and dilute to volume with ammonium oxalate-ammonium citrate solution. This solution should be prepared as needed.

Procedure

To the fourth fraction (approximately 270 ml), containing the tantalum, add 8 g of boric acid, 75 ml of hydrochloric acid, 80 ml of water, and 2 ml of zirconium sulfate solution. Warm on the steam bath (30° to 35° C) and stir occasionally to dissolve the boric acid. Cool to 5° C and add slowly, with continuous stirring, 25 ml of cupferron solution. Add paper pulp, stir well to distribute the pulp and allow the solution to stand 10 to 15 min. Filter through a double thickness of 7-cm close-texture paper fitted to a Büchner funnel. Transfer the precipitate to the filter, and wash well with 400 ml of cupferron wash solution. Transfer the paper and precipitate to a porcelain crucible, and ignite at a low temperature (500° to 550° C). Add 1 g of potassium pyrosulfate to the crucible, and fuse to dissolve the mixed oxides. Transfer the crucible and melt to a 100-ml beaker, and dissolve the melt in 25 to 50 ml of warm ammonium oxalate-ammonium citrate solution. The fusion should be agitated with a stirring rod while dissolving, in order to prevent a localized high concentration of tantalum which might lead to the precipitation of the hydrous oxide. Transfer the solution to a 50- or 100-ml volumetric flask and dilute to volume with ammonium oxalate-ammonium citrate solution. Transfer with a pipet 25 ml of pyrogallic acid solution to a 50-ml volumetric flask. Transfer a suitable aliquot, not to exceed 25 ml and containing not more than 1 mg of tantalum, to the flask, and mix well.

Dilute to volume with the ammonium oxalate-ammonium citrate solution, mix thoroughly, and allow to stand 10 min. Place water in a 2-cm photometer cell for use as a reference solution. Transfer a portion of the test solution, prepared as above, to a matched 2-cm photometer cell. Using the reference solution, adjust the photometer to the initial setting using a light band centered at 400 mμ. While maintaining this photometer adjustment, take the photometric reading of the test solution.

Determine the amount of tantalum present in the test solution from a calibration curve prepared as follows: Transfer with a pipet 25 ml of pyrogallic acid solution to each of four 50-ml volumetric flasks. Transfer 0.0, 2.0, 5.0, and 10.0 ml of standard tantalum solution (125 μg/ml) to the 50-ml volumetric flasks, and continue as directed in the previous paragraph. Plot the photometric readings of the calibration solutions with respect to micrograms of tantalum. The solutions follow Beer's Law, but a blank is required to correct for the color contributed by the pyrogallic acid solution. Because of the variable quality of this reagent, the system

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of photometric readings is designed to allow poor-quality lots to be detected and discarded. The reaction has a negligible temperature coefficient, but is sensitive to changes in pyrogallic acid concentration under the conditions specified in the procedure.

If 20 mg or more of tantalum is involved, the determination can be conveniently completed by precipitation with cupferron as described in the first paragraph in this procedure. No zirconium addition is made, and the oxide is ignited at 1,000° C and weighed as tantalum pentoxide. Losses due to incomplete precipitation or solubility do not exceed 0.5 mg of tantalum.

4. Results

Gram portions of high-purity niobium and tantalum pentoxides were prepared from commercial oxides by column elution with hydrochloric-hydrofluoric acid mixtures, precipitation with cupferron and ignition. Spectrographic examination of the niobium pentoxide indicated the chief impurities were boron and silicon. A chemical test made by ignition, treatment with sulfuric and hydrofluoric acids, and ignition, indicated these impurities to be negligible when using the oxide to prepare synthetic mixtures. Small amounts of silver, copper, calcium, iron, magnesium and tin were detected spectrographically and estimated to be less than 0.01 percent. A similar examination of the tantalum pentoxide indicated the same impurities, and in addition a very small amount of aluminum. It is likely that at least a part of the impurities that would ordinarily be removed by column separation actually represent contamination from dust distributed by the central air-heating system, resulting from plastering and painting work done at various times in the building while this project was in progress.

The results obtained on a series of synthetic mixtures made to simulate combinations of interest are given in table 1. Titanium and zirconium were added to the solution of the sample as aliquots of standard sulfate solutions prepared from National Bureau of Standards titanium dioxide Standard Sample 154a and from the zirconium sulfate referred to in section 3.3.c. Since stable solutions of niobium and tantalum cannot be prepared except through the use of complexing agents, weighed portions of the oxides were added to the first ignited cupferron concentrate. This mode of operation is justifiable on the basis that an appreciable part of these elements exists in steel as relatively insoluble carbides and nitrides which in any case cannot be duplicated by synthetic solution mixtures. A proof of the concentration step for these two elements would require more sensitive methods; possibly the use of active tracers in preparing the steels or activation analysis of the filtrate would define the lower limit. Since satisfactory replication was obtained on steels containing as little as 10 ppm of either element, the limit to be established is quite low.

The values for titanium and tantalum shown in table 1 require little comment, the values being within the limits usually obtained from photometric determinations. The values for zirconium are slightly high, and illustrate the difficulties encountered in properly washing the zirconium phosphate precipitate [10, p. 569, footnote 20]. A gravimetric finish for this determination is preferred, as an ignited precipitate is available to examine spectrographically for hafnium. The values obtained on the larger quantities of niobium are slightly low, due to the loss of a few tenths of a milligram of niobium in the precipitation with cupferron from the eluate complexed with boric acid (section 3.3.c). Provisional certificate values for NBS Standard Sample 123b are: Niobium, 0.75 percent; tantalum, 0.20 percent; and titanium, 0.006 percent. These values are given to show that small additions of titanium and zirconium can be recovered satisfactorily from a stainless steel (type 347) matrix containing tungsten, molybdenum, niobium, and tantalum.

The method was designed to provide values for titanium, zirconium, niobium, and tantalum in the range of 0.001 to 0.5 percent, in the standardization of a group of spectrographic steel standards containing additions of 22 elements and the rare earths. A part of these data, as well as a few results obtained on three current NBS Standard Samples of steel, is shown in table 2. In general, these values show

TABLE 1. *Values obtained by the recommended procedure for titanium, zirconium, niobium, and tantalum on synthetic mixtures*

Sample[a] number	Weight of sample	Titanium		Zirconium		Niobium		Tantalum	
		Added	Found	Added	Found	Added	Found	Added	Found
	g	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
55d	.5	10.3	10.3	10.6	10.8	10.7	10.2	10.7	10.7
55d	5	1.2$_5$	1.2$_7$	26.4	26.7	25.2	[b] 24.9	0.50	0.51
55d	5	25.0	25.3	1.06	1.18	0.60	0.60	24.9	[b] 24.9
55d	5	29.8	29.4	0.52	0.64	26.3	[b] 26.1	0.25	0.28
55d	5	0.60	0.60	26.2	27.6	0.30	0.30	24.4	[b] 24.3
55d	25	.60	.61	0.52	0.53	25.8	25.4	25.1	25.3
55d	25	.25	.26	.53	.57	0.30	0.31	0.25	0.27
123b	10	.....	.54	.....	.05	.....	[b] 74.6	.....	19.7
123b	10	.....	.55	.....	.00	.....	75.1	.....	19.9
123b	10	1.25	1.78	1.00	1.01	.....	[c]	.....	[c]
123b	10	.....	0.54	0.56	6.57	.....	[b] 74.3	.....	[b] 19.5

[a] NBS Standard Sample.
[b] Determination finished gravimetrically.
[c] Not determined.

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TABLE 2. *Values obtained by the recommended procedure for titanium, zirconium, niobium, and tantalum in NBS Standard Samples of steel*

Sample number	Sample weight	Titanium		Zirconium (+Hf)		Niobium		Tantalum		Type of steel
		Certificate value	Found	Certificate value	Found	Certificate value	Found	Certificate value	Found	
	g	%	%	%	%	%	%	%	%	
101d	25	[a]	0.0076 .0075	[a]	<0.005 <.005	[a]	0.003 .003	[a]	<0.001 <.001	18Cr-9Ni
170a	10	[b] 0.28	.271 .271		.036 .036	[a]	<.001 <.001	[a]	<.001 <.001	Open-hearth steel
121c	10	[b] .42	.410 .412	[a]	<.005 <.005	[a]	.003 .003	[a]	<.001 <.001	18Cr-11Ni
462 and 1162	15	.037	.038 .037 .037	0.063	.065 .061 .064	0.096	.095 .098 .093	0.036	.036 .036 .036	Low-alloy steel
463 and 1163	10	.010	.010 .011 .012	[c]	.208 .195 .197	.195	.192 .199 .194	.15	.151 .157 .152	Low-alloy steel
465 and 1165	25	.20	.207 .206 .208	[d]	$.001_4$ $.000_2$	[c]	$.001_2$ $.001_4$ $.001_3$	.001	$.001_2$ $.001_0$ $.001_0$	Low-alloy steel
467 and 1167	10	.26	.260 .264 .264	0.094	.094 .092 .096	0.29	.286 .290 .287	.23	.230 .231 .225	Low-alloy steel
A	10	[f]	.056 .055 .056 .056	[f]	<.01 <.01 <.01 <.01	[f]	.498 .494 .491 .489	[f]	.022 .023 .022 .022	19-9 DL

[a] Value not certified.
[b] Provisional value.
[c] Value not certified because of uncertainty of spectrographic homogeneity of the sample.
[d] Value not certified because of poor performance of recommended method below 0.01 percent.
[e] Value not certified because spectrographic method not sufficiently sensitive at present.
[f] Preliminary segregation test samples of forthcoming standard.

satisfactory replication, except for zirconium in those materials containing less than 0.01 percent of zirconium.

A quite satisfactory correlation between the chemical values was also obtained in setting up spectrographic curves; the exceptions were zirconium in the range below 0.01 percent where the performance of the chemical method is poor, and niobium below 0.01 percent where the spectrographic method lacks sufficient sensitivity at present to be useful.

Sample "A" illustrates the application of the procedure to a high-temperature material containing appreciable percentages of molybdenum and tungsten. It has already been shown [6] that niobium, molybdenum, and tungsten can be separated by anion exchange in hydrochloric-hydrofluoric acid mixtures, and it is hoped to further investigate mixtures of these elements in high-temperature alloys.

5. References

[1] F. H. Burstall and A. F. Williams, Analyst **77,** 983 (1952).
[2] M. J. Cabell and I. Milner, Anal. Chim. Acta. **13,** 258 (1955).
[3] W. S. Clabaugh and R. Gilchrist, J. Am. Chem. Soc. **74,** 2104 (1952).
[4] T. R. Cunningham, Ind. Eng. Chem., Anal. Ed. **5,** 305 (1933).
[5] T. R. Cunningham, Ind. Eng. Chem., Anal. Ed. **10,** 233 (1938).
[6] J. L. Hague, E. D. Brown, and H. A. Bright, J. Research NBS **53,** 261 (1954) RP2542.
[7] J. L. Hague, E. E. Maczkowske and H. A. Bright, J. Research NBS **53,** 353 (1954) RP2552.
[8] J. L. Hague, ASTM Proc. **44,** 714 (1944).
[9] R. B. Hahn, Anal. Chem. **21,** 1579 (1949).
[10] W. H. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, Appl. Inorg. Analysis 2d ed., p. 588 (J. Wiley and Sons, Inc., New York, N. Y., 1953).
[11] L. Ikenberry, J. L. Martin, and W. J. Boyer, Anal. Chem. **25,** 1340 (1953).
[12] C. M. Johnson, Iron Age **157,** No. 15, 66 (1946).
[13] Silve Kallmann (Ledoux and Co., Teaneck, N. J.) private communication.
[14] K. A. Kraus and G. E. Moore, J. Am. Chem. Soc. **73,** 9 (1951).
[15] K. A. Kraus and G. E. Moore, J. Am. Chem. Soc. **73,** 2900 (1951).
[16] K. A. Kraus and F. Nelson, Proc. Intern. Conf. Peaceful Uses Atomic Energy **7,** p. 116 (United Nations, N. Y., 1956).
[17] C. A. Kumins, Ind. Eng. Chem., Anal. Ed. **19,** 376 (1947).
[18] L. A. Machlan and J. L. Hague, J. Research NBS **59,** 415 (1957) RP2812.
[19] W. R. Schoeller, Analytical chemistry of tantalum and niobium, p. 1 (Chapman and Hall, Ltd., London, 1937).
[20] W. R. Schoeller and A. R. Powell, The analysis of minerals and ores of the rarer elements, 3d. ed., p. 210 (Hafner Publishing Co., New York, N. Y., 1955).
[21] G. Telep and D. F. Boltz, Anal. Chem. **24,** 163 (1952).

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Preparation of New Solution Standards of Radium

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New radium-solution standards have been prepared in the ranges of 10 micrograms and also 10^{-9} and 10^{-11} gram of radium element. These have been compared with the National Bureau of Standard's 1940 and 1947 series of radium-solution standards and, as a result of these comparisons, it has been found that the 1940 10^{-9} and 10^{-11}-gram solution standards contained some 2 to 3 percent more radium element than certified. It has been shown that this difference probably arose in the dilution of the 1940 standards.

1. Introduction

Radium-solution standards have previously been prepared at the National Bureau of Standards in 1940 and 1947. The 1940 series consisted of standards in the microgram range, ranging from 0.1 to 100.0 μg of radium element in 5 ml of solution, and standards for radon calibration consisting of 10^{-9} and 10^{-11} g of radium element in 100 ml of the radium-salt and carrier solution. The 1947 series consisted only of microgram standards ranging from 0.1 to 100.0 μg of radium element in 5 ml of solution of the radium bromide and nitric acid acting as carrier.

Recently the stock of 10^{-9}-g radium-solution standards became so depleted that it was necessary to prepare a new set of standards which has been designated as the 1957 series of standards and which consists chiefly of 10^{-9} and 10^{-11}-g standards with a few microgram standards which were prepared for comparison purposes. A new set of "blank solutions" was also prepared consisting of 100-ml samples containing 0.2 percent by weight of $BaCl_2 \cdot 2H_2O$.

2. Radium Calibration

A sample of radium chloride containing approximately 10 mg of radium element was returned to the Radium Chemical Company for a reseparation from radium D and its products and for recrystallization. It was requested that the radium salt should be crystallized in such a manner that the grain size would be of the same approximate dimensions as those in the Hönigschmid radium standards (which were also radium chloride) and that the radium salt should be enclosed in a glass tube of about the same dimensions (length, diameter, and wall thickness) as the tubes used by Hönigschmid. It would then be possible to compare this radium source with the two United States primary radium standards [1,2],[1] using the NBS gold-leaf electroscope [3], without making any absorption corrections. In such a comparison the sources are supported horizontally and then gently tapped so as to spread the grains of salt uniformly along the glass tubes.

While the radium source was compared in this manner with the two primary standards, this comparison was only treated as confirmation for a series of microcalorimetric comparisons which were carried out using the NBS radiation balance [4, 5]. These measurements consisted of three measurements of the rate of energy emission from the new radium source alone and also one triad of measurements [1, 2] of the new source relative to both primary standards (No. XIV and XV). The results of these measurements are shown in table 1.

TABLE 1. *Radiation-balance results for comparison of new radium source with the United States primary radium standards*

Date of measurement	Rate of energy emission in microwatts from—			Milligrams of radium element in new source
	No. XIV	No. XV	New source	
October 23, 1956	------	------	914.8	6.108
November 1, 1956	------	------	914.8	6.108
November 8, 1956	------	------	914.6	6.107
November 28, 1956	5728.0	3060.3	914.1	6.104

In calculating the values shown in table 1 a correction was made for the growth of polonium-210 in the national standards since June 1934. The mean value of the rate of energy emission from the new source is 914.6 μw which corresponds to 6.10_7 mg of radium element as of November 1956. The gamma-ray comparison, carried out with the gold-leaf electroscope, gave an average value from twelve measurements equal to 6.08 mg of radium element.

3. Preparation of the New Radium-Solution Standards

The 6.10_7-mg radium source was now completely shattered at the bottom of a 5-liter thick-bottomed glass bottle under 3.052 liters of carrier solution, determined by weighing and consisting of 0.2-percent $BaCl \cdot 2H_2O$ plus 5-percent HCl, by imparting a sharp blow to the glass tube by means of a specially constructed glass rod with a thickened and elongated end which was struck at its other end with a hammer. By this procedure the master solution of radium and carrier, with a concentration of radium element of 2.001×10^{-6} g/ml, was prepared.

The dilutions that were made from this master solution are shown diagrammatically in figure 1. These dilutions were carried by two independent routes, designated as A and B, in order to check the accuracy of dilution. The master solution as well as all subsequent dilutions thereof were thoroughly

[1] Figures in brackets indicate the literature references at the end of this paper.

mixed by agitation before aliquots were removed. All glassware used was carefully calibrated.

First of all two 10-ml aliquots were each diluted to 100 ml in a 100-ml volumetric flask using carrier solution. Following this, eight 5-ml aliquots were pipetted into glass ampoules and flame-sealed. These eight ampoules each containing 10.16_3 μg of radium-226 per 5.079 ml of solution were set aside for comparison with the microgram range of both the 1940 and 1947 standards by means of the NBS $4\pi\gamma$-ionization chamber.

At this point the remainder of the master solution was siphoned off into two 2,500-ml volumetric flasks and flame sealed for future possible use. The remaining small volume containing the fragments of the glass tube was checked and found to contain no more radium per milliliter than one of the 10-μg samples.

The further dilutions along routes A and B were carried out as shown in figure 1 and gave, by each route, fifty 10^{-9}-g and fifty 10^{-11}-g radium 100-ml solution standards. Of these the first, twenty-fifth, and fiftieth 10^{-9}-g and 10^{-11}-g ampoules in both route A and route B were reserved for later comparison with the 1940 series of 10^{-9}-g and 10^{-11}-g radium-solution standards. The nominal values of the dilutions shown by each route were: 2×10^{-7}g/ml, 2×10^{-9}g/ml, 1×10^{-11}g/ml, and 1×10^{-13}g/ml.

Four of the eight 1957 10-μg radium standards were now compared in the NBS $4\pi\gamma$-ionization chamber [6, 7] with four 10-μg radium-solution standards of the 1947 series and were found to agree with the 1947 values to within the ±1 percent estimated accuracy of the 1947 standards. Subsequently three of the 1940 series of 10-μg radium-solution standards, the stock of which had been believed to be exhausted, were found and compared with three of the 10-μg standards of the 1947 series and three of the 1957 series.

Due to the quite large calibration correction of the 5-ml pipet (the volume was equal to 5.079 ml) the nominal 1957 10-μg radium-solution standards have an actual radium content of 10.16_3 μg. The comparisons of the 1957 standards with the 1947 standards were carried out in April and August 1957, while that of the 1957 with the 1940 10-μg standards was carried out in August 1957.

The certified values of both the 1940 and 1947

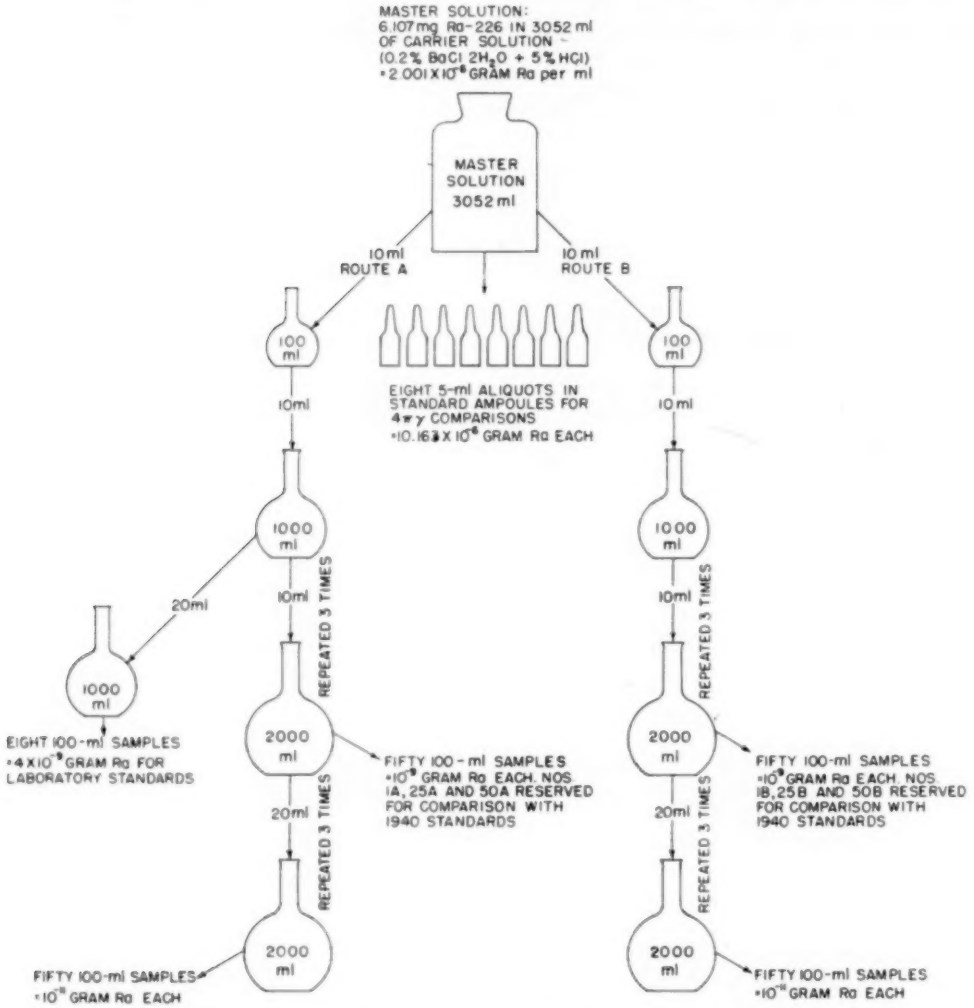
MASTER SOLUTION:
6.107 mg Ra-226 IN 3052 ml
OF CARRIER SOLUTION -
(0.2% BaCl 2H2O + 5% HCl)
=2.001 X 10⁻⁶ GRAM Ra per ml
MASTER SOLUTION 3052 ml
10 ml ROUTE A
10 ml ROUTE B
100 ml
EIGHT 5-ml ALIQUOTS IN STANDARD AMPOULES FOR 4πγ COMPARISONS
=10.16₃ X 10⁻⁶ GRAM Ra EACH
10ml
1000 ml
20ml
10ml
REPEATED 3 TIMES
2000 ml
20ml
EIGHT 100-ml SAMPLES
=4 X 10⁻⁹ GRAM Ra FOR LABORATORY STANDARDS
FIFTY 100-ml SAMPLES
=10⁻⁹ GRAM Ra EACH. NOS. 1A, 25A AND 50A RESERVED FOR COMPARISON WITH 1940 STANDARDS
FIFTY 100-ml SAMPLES
=10⁻¹¹ GRAM Ra EACH
FIFTY 100-ml SAMPLES
=10⁻⁹ GRAM Ra EACH. NOS. 1B, 25B AND 50B RESERVED FOR COMPARISON WITH 1940 STANDARDS
FIFTY 100-ml SAMPLES
=10⁻¹¹ GRAM Ra EACH

FIGURE 1. *Dilution scheme for the preparation of 1957 10^{-9}-g and 10^{-11}-g radium standards.*

"10-μg" radium-solution standards are 10 μg as of August 1940 and May 1947, respectively.

In terms of the 1940 10-μg radium standards the 1957 "10-μg" standards were found to contain 10.150 $\pm$0.0014 μg of radium in August 1957. This value is in terms of different 1940 ampoules and the agreement is well within the almost $\pm$1 percent uncertainty of the values of the 1940 standards.

In terms of the 1947 10-μg radium standards the 1957 "10-μg" standards were found, in the August 1957 measurements in the NBS $4\pi\gamma$-ionization chamber, to have a radium content of 10.230 μg in contrast to the calibrated value of 10.16_3 μg. This value is again within the almost $\pm$1 percent uncertainty of the 1947 standards.

Finally a number of the 20-μg and 50-μg standards of the 1947 series were compared with those of the 1940 series. The complete series of $4\pi\gamma$-ionization-chamber measurements is summarized in figure 2 where, on the left-hand side the results of the comparisons of the 1940 to 1947 standards are shown. In this case both the 1940 and 1947 standards are certified as 10, 20, and 50 μg. The small errors indicated are those to be associated with the $4\pi\gamma$-ionization-chamber measurements while the larger errors are those inherent in both the 1940 and 1947 standards. Within these latter limits there is no deviation from unity.

On the right-hand side the ratio of the four 1957 to seven 1947 10-μg standards is shown, *after correcting* for the volume of the 5.079-ml pipet (used in the 1957 series) to the equivalent of the 5 ml (i. e., correcting to 10.000 μg instead of 10.16_3 μg for the 1957 series). After this correction has been made the ratio of the 1947 series (certified simply as 10 μg) to the 1957 series should be unity. Once again the deviation from unity (1.0054 $\pm$0.0004, the error of the $4\pi\gamma$-ionization-chamber measurement) is well within the 0.8 percent "uncertainty" certified in the case of the 1947 series of radium-solution standards above, without even considering the errors inherent in the 1957 series which are estimated to total about $\pm$0.1 percent or 0.2 percent. The actual precision in four microcalometric comparisons of the 6-mg radium preparation with the national radium standards was such as to give a standard deviation of the average of 0.02 percent.

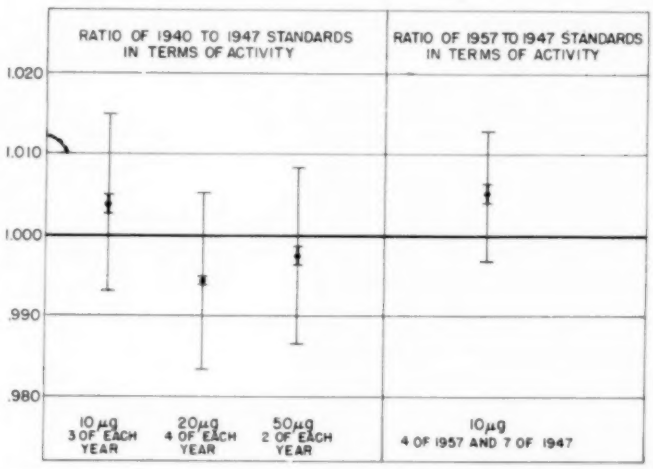
RATIO OF 1940 TO 1947 STANDARDS IN TERMS OF ACTIVITY
RATIO OF 1957 TO 1947 STANDARDS IN TERMS OF ACTIVITY
1.020
1.010
1.000
.990
.980
10μg 3 OF EACH YEAR
20μg 4 OF EACH YEAR
50μg 2 OF EACH YEAR
10μg 4 OF 1957 AND 7 OF 1947

FIGURE 2. *Comparisons of the activities of the 1940, 1947, and 1957 radium gamma-ray standards.*

4. Comparison of the 1940 and 1957 10^{-9}-g Radium-Solution Standards by the Method of Radon Analysis

The method of radon analysis in use at the National Bureau of Standards is essentially the method described by Curtiss and Davis [8, 9], but with the reflux condensers for de-emanation of the radium solution standards replaced by wash bottles with sintered-glass filters as described by Harding, Schwebel, and Stockmann [10]. The radon is removed from these solutions by means of a fine stream of nitrogen bubbles passing through the solutions from the sintered-glass filters. In order to confirm the results obtained with this method of de-emanation the reflux condensers were, however, reinstalled for a final set of comparisons.

Because of the somewhat lower precision of the radon method of analysis, as compared with the gamma-ray measurements already described, a most exhaustive series of intercomparisons between the 1940 and 1957 series of standards was carried out by the radon method.

As indicated in figure 1 ampoules 1A, 25A, 50A, 1B, 25B, and 50B were selected from the 1957 dilutions for comparative measurements.

Four 100-ml ampoules, designated as A, B, C, and D, were available from the 1940 10^{-9}-g radium-solution standards and were used to compare with the six 1957 ampoules.

The 1940 10^{-9}-g standards were certified just as 10^{-9}g of radium element. The certified value for the 1957 standards is 0.999×10^{-9}g of radium. The ratio of activities of the 1940 and 1957 standards was now determined by using each in turn to calibrate eight NBS alpha-particle-pulse-ionization chambers [8, 9] that are routinely used for radon assays. The results were expressed in terms of the ratio of the activity of the 1957 radium-solution standards, as determined by the calibration (in terms of counts per unit of radon) of any given chamber to that of the 1940 radium-solution standards corrected for radium decay, using the same chamber, and are shown in table 2 (a).

TABLE 2 (a). *Comparison of 1957 and 1940 10^{-9}-g standards*

(The entries are the result of dividing the activities of the 1957 standard by those of the 1940 standards)

1940 Standards	1957 Standards					
	1A	25A	50A	1B	25B	50B
A	0.970	0.964	0.971	0.970	0.975	0.974
B	.987	.958	.980	.974	.987	.964
C	.982	.969	.983	.980	.962	.964
D	.983	.977	.965	.980	.976	.980

Average ratio 1957/1940=0.9740
Standard deviation of the average of 24 ratios=0.0018

The average ratio of 0.9740 derived from the results of table 2 (a) for the 1957 and 1940 standards indicates that the certified radium content of the 1940 standards was low by 2.6 percent.

Subsequently eight reflux condensers were reinstalled for de-emanation of the standard solutions by boiling. The radon was fed from two of these reflux condensers into two of the eight alpha-particle-ionization chambers that had been used to obtain the results in table 2 (a). The values for the ratio obtained for the 1957/1940 activities (again obtained from the chamber calibrations) using the reflux condensers, and again corrected for decay, are shown in table 2 (b). These last results were not, however, used in calculating the average ratio of 0.9740 as they were not systematically determined for every combination of the 1957 standards (1A, 25A, 50A, 1B, 25B, and 50B) on the one hand and the 1940 standards (A, B, C, and D) on the other. The reflux-condenser measurements were merely confirmatory.

TABLE 2 (b). *Comparison of 1957 and 1940 10^{-9}-g standards using reflux condensers for de-emanation*

Ratio of activities of 1957 to 1940 standards			
1940 Standards	1957 Standards		
	50A	25B	50B
A	0.978	0.977	----
	.978	.975	0.984
B	.987	.986	----
D	.986	.985	.989
	.983	.980	----
Average ratio 1957/1940=0.9823			

This discrepancy of 2.6 percent was so large that it was considered desirable to check the 1940 and 1957 standards against the 1947 standards to try to determine which was the more likely to be in error.

Unfortunately, however, the 1947 series consists only of standards in the range of microgram quantities of radium element. It was, therefore, necessary to carry out a dilution of 1947-microgram standards to the 10^{-9}-g level. This was, however, accepted as an additional check on the accuracy of our dilution. The dilution scheme is shown in figure 3, the initial master solution consisting of six 10-μg radium-solution standards from the 1947 series. By taking six standards, each consisting of 5 ml of solution, the total error arising from the individual errors in volume of each of these standards should be proportionately lower. Once again dilutions were carried out by two alternate routes. Five samples were taken from each route and these were numbered as shown in figure 3. Again all glassware used was carefully calibrated. The nominal values of the dilutions were: 2×10^{-7} g/ml, 2×10^{-9} g/ml, and 1×10^{-11} g/ml.

The ratios of activities were now determined for the 1947 and 1940 10^{-9}-g samples and standards

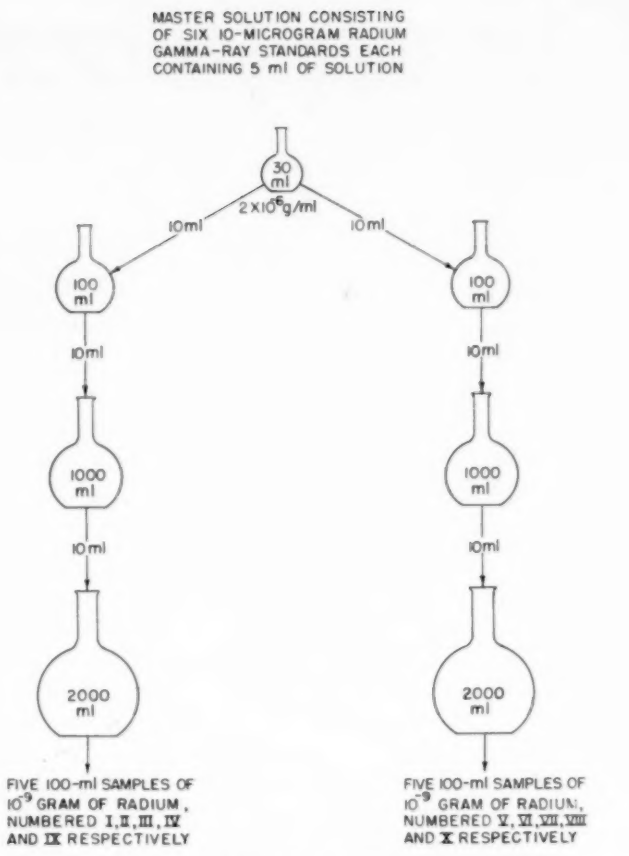
MASTER SOLUTION CONSISTING OF SIX 10-MICROGRAM RADIUM GAMMA-RAY STANDARDS EACH CONTAINING 5 ml OF SOLUTION
30 ml
2X10⁻⁶g/ml
10ml
10ml
100 ml
100 ml
10ml
10ml
1000 ml
1000 ml
10ml
10ml
2000 ml
2000 ml
FIVE 100-ml SAMPLES OF 10⁻⁹ GRAM OF RADIUM, NUMBERED I, II, III, IV AND IX RESPECTIVELY
FIVE 100-ml SAMPLES OF 10⁻⁹ GRAM OF RADIUM, NUMBERED V, VI, VII, VIII AND X RESPECTIVELY

FIGURE 3. *Dilution scheme for the preparation of 10^{-9}-g samples from 1947 radium gamma-ray standards.*

and for the 1947 and 1957 10^{-9}-g samples and standards with the results shown in tables 3 (a) and 4 (a), the appropriate corrections again being made for radium decay. The sintered-glass-filter method of de-emanation was used in these measurements and also the same eight alpha-particle-ionization chambers as were used to obtain the 1957/1940 ratios shown in table 2 (a). In view, however, of the greater numbers of 1940 and 1957 10^{-9}-g standards and 1947 10^{-9}-g samples involved it was not possible to compare every standard solution with every 1947 10^{-9}-g sample. A pattern of comparison was devised, as indicated in tables 3 (a) and 4 (a) to give a maximum number of interchecks without taking every possible combination. Once again a number of spot comparisons was carried out using the same alpha-particle-ionization chambers and reflux condensers as were used to make the measurements in table 2 (b) and the results of these spot comparisons, again corrected for radium decay, are shown in tables 3 (b) and 4 (b). These results, as they were less systematic, were not used in the deriving of the 1947/1940 and 1947/1957 averages of 0.9722 and 0.9878, respectively.

These results of 0.9722 (1947/1940) and 0.9878 (1947/1957), as compared with 0.9740 (1957/1940), do tend to show a weight of evidence against the 1940 series of 10^{-9}-g radium-solution standards.

TABLE 3 (a). *Comparison of 1947 10^{-9}-g samples and 1940 10^{-9}-g standards*

(The entries are the result of dividing the activities of the 1947 samples by those of the 1940 standards)

1940 Standards	10^{-9}-g solutions made from six 1947 10-μg gamma-ray standards							
	I	II	III	IV	V	VI	VII	VIII
A	0.976	0.966	-----	-----	-----	-----	0.967	0.956
B	-----	-----	0.970	0.980	0.967	0.973	-----	-----
C	.967	.972	-----	-----	.981	.970	-----	-----
D	-----	-----	.978	.972	-----	-----	.981	.980

Average ratio 1947/1940=0.9722
Standard deviation of the average of 16 ratios=.0018

TABLE 3 (b). *Comparison of 1947 10^{-9}-g samples and 1940 10^{-9}-g standards using reflux condensers for de-emanation*

Ratio of activities of 1947 to 1940 standards

1940 Standards	10^{-9}-g solutions made from six 1947 gamma-ray standards			
	I	II	V	VIII
A	0.966	0.960	0.962	0.965
	.972	.968	.964	-----
B	.981	.975	.976	.968
	-----	-----	-----	.978
D	.974	.968	.970	.967
	.977	.973	.969	.970

Average ratio 1947/1940=0.9702

TABLE 4 (a).—*Comparison of 1947 10^{-9}-g samples and 1957 10^{-9}-g standards (the entries are the result of dividing the activities of the 1947 samples by those of the 1957 standards)*

1957 Standards	10^{-9}-g solutions made from six 1947 gamma-ray standards							
	I	II	III	IV	V	VI	VII	VIII
1A	0.990	0.979	0.991	0.984	-----	-----	-----	-----
25A	-----	-----	.987	1.008	1.007	0.987	-----	-----
50A	-----	-----	-----	-----	0.993	.988	0.974	0.984
1B	-----	-----	.989	0.986	-----	-----	.981	.982
25B	.990	.986	-----	-----	.990	.983	-----	-----
50B	.993	.982	-----	-----	-----	-----	.988	.984

Average ratio 1947/1957=0.9878.
Standard deviation of the average of 24 ratios=0.0014

TABLE 4 (b).—*Comparison of 1947 10^{-9}-g samples and 1957 10^{-9}-g standards using reflux condensers for de-emanation*

Ratio of activities of 1947 to 1957 standards

1957 Standards	10^{-9}-g solutions made from six 1947 gamma-ray standards			
	I	II	V	VIII
50A	0.988	0.990	0.984	0.986
	.993	-----	-----	-----
25B	0.996	0.983	0.988	0.989
	.989	.993	.985	-----
50B	0.987	0.984	-----	0.980

Average ratio 1947/1957=0.9885

The direct measurements of the ratios for the standards and samples for the different years are therefore:

1947/1940=0.9722	1940/1947=1.0286
1940/1957=1.0267	1957/1940=0.9740
1957/1947=1.0124	1947/1957=0.9878

Product of 3 ratios=1.0124 =0.9896 [2]

The three estimates, if completely consistent, should multiply together to give exactly unity. The slightly less than 1-percent uncertainty in the individual ratios accounts for this discrepancy.

The three estimates may be slightly adjusted by a least-squares technique to give estimates that are consistent. For example, in addition to the direct estimate of the 1957/1947 ratio (1.0124) an indirect estimate may be obtained by multiplying the estimate for 1957/1940 by the estimate for 1940/1947. The result of multiplying 0.9740 by 1.0286 is 1.0019. Most weight must be given the directly obtained value of 1.0124. The proper average is obtained by taking the cube root of the product of the square of the directly observed ratio by the indirectly estimated ratio for 1957/1947. Thus

$$\sqrt[3]{1.0124\times1.0124\times1.0019}=1.0089.$$

The adjusted estimates of the ratios between standards and samples for different years, obtained by this least squares technique are:

1947/1940=0.9688	1940/1947=1.0322
1940/1957=1.0231	1957/1940=0.9774
1947/1947=1.0089	1947/1957=0.9912

Product of 3 ratios=1.0000 =1.0000

The adjustments do not exceed twice the estimated standard deviation in the direct estimates of the ratios. The standard deviation of the average ratios listed in tables 2, 3, and 4 is slightly less than 0.2 percent. These adjusted values combine all the evidence and are the preferred ratios.

5. Comparison of the 1940 and 1957 10^{-11}-g Radium-Solution Standards by the Method of Radon Analysis

As a further check between the 1940 and 1957 series of standards three 1940 10^{-11}-g radium-solution standards of 100 ml, certified as containing 1.025×10^{-11}g and designated as 11, 12, and 13, were compared with three 1957 10^{-11}-g radium-solution standards of 100 ml, designated as 21, 22, and 23 and found to contain 1.001×10^{-11}g, by the method of radon analysis using alpha-particle-ionization chambers 7 and 12 and de-emanating by boiling in the reflux condensers.

In view of the longer collection times that were involved and the fact that the readings were only some ten times background the results took much

[2] The reciprocals of the ratios as determined from the original values are shown for convenience in computation, should they be desired.

longer to obtain and it was not, therefore, possible to carry out as exhaustive comparisons as with the 10^{-9}-g standards. The results, after correction for radium decay, are shown, however, in table 5. The average ratio of 0.986 (1957/1940), with a standard deviation of the average of 0.020, is in fairly close agreement with the value of 0.9774 (1957/1940) for the adjusted ratio for the 10^{-9}-g radium-solution standards. It must, however, be borne in mind that additional errors are introduced at such low concentrations as 10^{-11}-g radium per 100 ml by uncertainties in the radium content of the diluting carrier solution, as will be apparent from measurements made on such solutions which will now be described.

TABLE 5. *Comparison of 1959 and 1940 10^{-11}-g standards using reflux condensers for de-emanation*

Standard No.[a]	Radium content in units of 10^{-11}g	
	Chamber No. 7	Chamber No. 12
11	1.040	-----
21	-----	1.032
12	1.001	-----
22	-----	1.016
11	-----	1.047
21	1.022	-----
12	-----	1.007
13	1.032	-----
23	-----	0.990
13	-----	1.018
23	1.012	-----
22	0.987	-----
Average ratio 1957/1940=0.986		
Standard deviation=0.020		

[a] 1940 Standards designated as 11, 12, and 13; 1957 Standards designated as 21, 22, and 23.

6. Determination of the Radium Content of the Carrier Solution

The carrier solution used in the dilutions, shown schematically in figures 1 and 3, consisted of 0.2 percent by weight of $BaCl_2 \cdot 2H_2O$. In order to determine the radium content of this carrier solution, 31 g of the barium chloride used in its preparation was dissolved in 100 ml of radium-free distilled water and this solution was then analyzed for radium by the radon method. Three measurements of this sample gave values of 0.1245, 0.1258, and 0.1261×10^{-12}g, or an average of 0.1255×10^{-12}g, radium per gram of $BaCl_2 \cdot 2H_2O$. Thus a 100-ml sample of the 0.2 percent by weight barium chloride carrier solution would contain a total of 0.025×10^{-12}g of radium.

There is no record of the method of measuring the 1940 blank solutions certified as containing 0.25×10^{-12}g of radium per 100 ml. Attempts were made, however, to measure by the radon method the radium content of both 1940 and 1957 blank solutions. These attempts resulted in a wide range of values being obtained, some of which were as much as ten times greater, in the case of the 1957 blank solutions, than the value obtained from the measurements of the nearly saturated solution of barium chloride.

These variations reflect the limitations of the radon method for measurements which are, in this case, of the order of one-tenth background. The average value obtained, however, for the 1940 blank solutions was 0.18×10^{-12}g of radium per 100 ml as compared with the certified value of 0.25×10^{-12}g of radium per 100 ml.

It appears that the 1940 10^{-11}-g radium-solution standards which are certified as containing 1.025×10^{-11}g of radium were derived from the dilution of the 10^{-9}-g radium solution, certified as containing 10^{-9}g of radium per 100 ml, with the blank solution which was said to contain 0.025×10^{-11}g of radium per 100 ml. If this last figure were obtained, however, by the radon method it would appear to be no more reliable than that of 0.18×10^{-12}g of radium per 100 ml recently determined.

Under these circumstances the value of 0.986 obtained for the ratio of the 1957/1940 10^{-11}-g radium solution standards cannot be said to differ significantly from that of 0.977 obtained for the ratio of the 1957/1940 10^{-9}-g radium-solution standards.

7. Summary

From the measurements on the 1940 and 1957 10^{-9}-g radium-solution standards, which are confirmed by those of the 10^{-11}-g series, it would appear that there is an error of about 2.6 percent in the 1940 series of 10^{-9}-g and 10^{-11}-g radium-solution standards. As no corresponding discrepancy has been observed in the microgram series of standards it is assumed that the error is one which occurred in the dilution down to 10^{-9}g and 10^{-11}g per 100 ml in 1940.

8. References

[1] T. I. Davenport, C. C. McCraven, W. B. Mann, and C. C. Smith, Comparison of four national radium standards, Part 1. Experimental procedures and results; W. S. Connor and W. J. Youden, Part 2. Statistical procedures and survey, J. Research NBS **53,** 267 (1954) RP2544.

[2] T. P. Loftus, W. B. Mann, L. Paolella, L. L. Stockmann, and W. J. Youden, Comparisons of national radium standards, J. Research NBS **58,** 169 (1957) RP2749.

[3] L. F. Curtiss, A projection electroscope for standardizing radium preparations, Rev. Sci. Instr. **16,** 363 (1928).

[4] W. B. Mann, Use of Callendar's "radio-balance" for the measurement of energy emission from radioactive sources, J. Research NBS **52,** 177 (1954) RP2486.

[5] W. B. Mann, A radiation balance for the microcalorimetric comparison of four national radium standards, J. Research NBS **53,** 277 (1954) RP2545.

[6] C. C. Smith and H. H. Seliger, Improvement in response of 4π-gamma-ionization chambers, Rev. Sci. Instr. **24,** 474 (1953).

[7] S. B. Garfinkel, Semi-automatic Townsend Balance system (submitted for publication).

[8] L. F. Curtiss and F. J. Davis, A counting method for the determination of small amounts of radium and radon, J. Research NBS **31,** 181 (1943) RP1557.

[9] F. J. Davis, Factors affecting operation of apparatus for counting alpha particles in an ion counting chamber, J. Research NBS **39,** 545 (1947) RP1846.

[10] J. E. Harding, A. Schwebel, and L. L. Stockmann, Report on the determination of small amounts of radium in solution, AOAC **41,** 311 (1958).

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Phase Equilibrium Relations in the Binary System Lead Oxide-Niobium Pentoxide

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The phase equilibrium diagram for the binary system lead oxide-niobium pentoxide has been constructed from observations of fusion characteristics and X-ray diffraction data. The system contains six binary compounds with $PbO:Nb_2O_5$ ratios of 3:1, 5:2, 2:1, 3:2, 1:1, and 1:2. The compound $PbO \cdot Nb_2O_5$ was found to melt congruently at 1,343° C and have a stable, reversible phase transformation temperature from the low-temperature rhombohedral form to the high-temperature tetragonal form at 1,150° C. The 5:2, 2:1, and 1:2 compounds melt congruently at 1,220°, 1,233°, and 1,337° C, respectively; the 3:1 and 3:2 compounds melt incongruently at 985° and 1,233° C, respectively.

1. Introduction

A study of phase relationships in the binary system PbO-Nb_2O_5 has been conducted as part of a program of fundamental phase equilibria studies of ceramic materials. The compounds $PbO \cdot Nb_2O_5$ and $2PbO \cdot Nb_2O_5$ have been previously reported by Goodman [1],[1] and a phase transformation in the $PbO \cdot Nb_2O_5$ compound has been reported by Francombe [2]. Cook and Jaffe [3, 4] have studied $2PbO \cdot Nb_2O_5$ and compositions deficient in PbO and report a cubic phase to occur at a composition of $3PbO \cdot 2Nb_2O_5$. However, no systematic attempt has been made to study the phase-equilibrium relations in the entire binary system.

X-ray diffraction data, together with the determination of the melting points of the compounds and of the solidus and liquidus temperatures at various compositions across the system, have supplied data from which an equilibrium diagram has been constructed.

Because of the volatility of PbO, many of the experiments were conducted in sealed Pt tubes. As PbO tends to vaporize markedly at the temperature studied, all the data may not be exactly equivalent to the true values at atmospheric pressure. However, as these experiments could not be conducted in air and the pressure inside the tube was relatively small, it is felt that the data show the best available approach to the equilibrium conditions prevailing under atmospheric pressure.

2. Sample Preparation and Test Methods

The following starting materials were used in the preparation of samples:

PbO—Reagent grade yellow lead oxide. This material was found by X-rays to contain only the high-temperature modification of PbO, massicotite, and none of the tetragonal red lead oxide, lithargite. Spectroscopic analyses showed 0.01 to 0.1 percent Co, 0.001 to 0.01 percent Bi and Tl, 0.0001 to 0.001 percent Ag, Al, Ca, Cu, and Si and less than 0.0001 percent Mg.

Nb_2O_5—High-purity grade niobium pentoxide, over 99.7 percent. Spectroscopic analyses showed 0.01 to 0.1 percent Zr, 0.001 to 0.01 percent Fe and Si, and 0.0001 to 0.001 percent Ca and Mg.

Calculations of weight composition were made to ±0.01 percent, no correction being made for the percentage purity of the raw materials, except for a factor due to weight lost on ignition. The starting materials, in sufficient quantities to give a 5.0-g sample, were weighed to the nearest 0.1 mg. They were then mixed by hand, tumbled for 1 hr, ground for 1 hr in an agate mortar, and formed into ⅝-in.-diam disks at a pressure of 10,000 lb/in.². The pressed disks were fired for 1 hr at 750° C on platinum foil in an air atmosphere, using an electrically-heated furnace wound with 80 percent Pt–20 percent Rh wire.

Following the preliminary heat treatment, the disks were ground, and for those specimens selected for the X-ray study new disks about ¼ in. high were formed at 15,000 lb/in.² in a ½-in.-diam mold and refired for ½ to 1 hr at various appropriate temperatures between 800° C and 1,400° C. In order to reduce PbO loss, a system of inverted Pt crucibles similar to that reported by Jaffe, Roth, and Marzullo [5] was utilized. For those specimens which still indicated appreciable weight loss, a sealed Pt tube, containing a small amount of the ground, calcined mixture, was quenched from the appropriate temperature. Equilibrium conditions, except in the immediate vicinity of a phase transformation, could usually be obtained in the sealed tube in 10 to 15 min. X-ray diffraction powder patterns were made, using a high-angle recording Geiger-counter Spectrometer and Ni filtered Cu radiation, with the Geiger counter traversing the specimen at ¼°/min and the radiation being recorded on the chart at 1° 2θ/in.

Specimens for solidus and liquidus determinations were mixed with a few drops of a 20-percent solution of polyethylene glycol in water, pressed into disks in the same manner as for the X-ray specimens, and ground in the form of small four-sided pyramids grooved on each side as described by Geller et al. [6]. Solidus and liquidus determinations were made in

[1] Figures in brackets indicate the literature references at the end of this paper.

the electrically heated furnace using a Pt versus 90 Pt–10 Rh thermocouple and an indicating potentiometer for temperature measurements. The specimens were placed on a Pt disk which was on a support of mullite. An oxidizing atmosphere existed in the furnace at all times. The specimens were placed around the circumference of a circle, 1 in. away from the thermocouple, maintained at temperature for ½ hr, and allowed to cool by shutting off the furnace. The solidus and liquidus temperatures were arrived at by visual inspection of the cooled specimen. The solidus temperature was recorded as the first sign of liquid formation, as indicated by rounding of the corners of the test pyramid. The temperature of complete melting, as indicated by the formation of a flat button, was recorded as the liquidus temperature. In all cases many tests had to be made to determine these two values.

In general, this pyramid method was only usable for those specimens containing less than 50 percent of PbO. Specimens containing more than 50 percent of PbO tended to change composition rapidly when heated in air and it was necessary to seal these compositions in small Pt tubes. For specimens which had been heated in the sealed tubes, visual observation of partial melting of the quenched specimens could usually locate the solidus temperature. In some cases, the appearance of a new phase in the X-ray pattern with different heat treatments was the best means of locating the solidus. The liquidus temperatures could probably be found only by detailed optical microscope examination. No attempt has been made to locate accurately the liquidus temperatures in that portion of the system containing greater than 50 percent of PbO.

The methods of determination of temperature limits of a particular phase are subject to a number of sources of error. Among these are the possible introduction of impurities into the specimens in the forming and grinding operations, the possibility of reduction of Nb_2O_5, oxidation and/or differential loss of PbO, difference of temperature between one or more specimens and the thermocouple, and the inherent difficulty in the visual determination of the solidus and liquidus temperatures. It is believed that the temperatures as recorded are accurate to $\pm 5°$ C.

3. Compounds Involved in the PbO–Nb_2O_5 System

3.1. Nb_2O_5

Brauer [7] has found Nb_2O_5 to occur in three polymorphic forms. The H-form or high-temperature form was reported as stable at temperatures above 1,200° to 1,250° C. In this study wherever free Nb_2O_5 was found, the high-temperature form was the one observed in all heated specimens, although the low-temperature form was used as the starting material. Holzberg, Reisman, Berry, and Berkenblit [8] concluded that Nb_2O_5 has only two crystalline polymorphs, the high- and the low-temperature forms, with an irreversible phase transformation, γ to α (low to high) at 830° C. They gave the parameters of the high-temperature form as, monoclinic, $a=21.34$ A, $b=3.816$ A, $c=19.47$ A, and $\beta=120° 20'$. Magneli and Lagergren [9] have used the parameters $a=21.50$ A, $b=3.825$ A, $c=20.60$ A and $\beta=121° 45'$. Holzberg et al. have indexed the diffraction peak at 1.915 A as (712). The index of this peak should probably be (020). Holzberg [10] has agreed that the b value of 3.825 A is probably more correct. Table 1 shows the indexed X-ray pattern of high-temperature Nb_2O_5, as found in the present study, compared with the indexed values shown by Holzberg et al. [8] and Magneli and Lagergren [9]. The parameters found for the material used in the present study are $a=21.08$ A, $b=3.823$ A, $c=19.33$ A, and $\beta=119° 48'$.

3.2. PbO

PbO occurs in two polymorphic forms. The low-temperature form, stable at room temperature, is lithargite, red PbO, tetragonal with $a=3.976$ A, $c=5.023$ A [11]. It transforms to massicotite, yellow lead oxide, at 489° C [12]. Yellow PbO is orthorhombic, and the material used for the present study has the parameters $a=5.48$ A, $b=5.88$ A, $c=4.75$ A. The high-temperature polymorph is found to exist, metastably, at room temperature when quenched from any temperature in the sealed Pt tube. Even 65 hr at 470° C, just below the transformation temperature, showed no sign of red PbO. Petersen [12] has shown that it takes two to three weeks at 420° to 430° C to convert the yellow lead oxide into the red form.

3.3. Compound PbO·Nb_2O_5

The compound PbO·Nb_2O_5 has been reported to occur in four different symmetry modifications.[2] The compound was first described by G. Goodman [1] as ferroelectric, orthorhombic. Francombe [2] first reported a low-temperature rhombohedral phase, and Roth [14] showed that a tetragonal modification probably also existed. Cook [15] has indicated that a pyrochlore-type phase is present if the material is not heated above 700° C.

a. Low-Temperature Rhombohedral Modification

Francombe [2] reported that the compound PbO·Nb_2O_5 was polymorphic, having a phase transformation at about 1,200° to 1,250° C. The low temperature form is not ferroelectric and was reported to be rhombohedral with the "simplest-structure-cell" possessing the dimensions $a_R=6.206$ A and $\alpha_R=58° 18'$. However, the X-ray powder pattern given by Francombe [2] was indexed on a larger "pseudo-cubic-cell" with dimension $a'_R=8.664$ A and $\alpha'_R=88° 30'$.

[2] A paper in Russian by Efimov et al. [13] discusses the reactions involved in producing PbO·Nb_2O_5 and reports a face centered cubic lattice of 5.277 A for this compound. As only an abstract of this paper was available in English, this result cannot be critically analyzed. However, it seems likely that the X-ray pattern giving rise to this data was of the pyrochlore-type structure occurring at a ratio of 3PbO to 2Nb_2O_5, which has a parameter of approximately twice that given in the Russian work.

TABLE 1. *X-ray powder diffraction data for high temperature* Nb_2O_5

Magneli and Lagergren [9]			Holzberg et al. [8]			Present work CuK_{α_1} radiation				
d_{obs}	I/I_0	hkl[a]	d_{obs}	I/I_0	hkl[b]	d	I/I_0	$1/d^2_{obs}$	$1/d^2_{calc}$ [c]	hkl[d]
17.0	30	$10\bar{1}/001$	16.9	10	001	16.66	6	0.0036	0.0036	001
10.6	40	$20\bar{1}$	10.6	20	$20\bar{1}$	10.517	5	.0090	.0090	$20\bar{1}$
						10.063	2	.0099	.0099	101
9.7	10	$10\bar{2}$	9.7	10	$10\bar{2}$	9.615	2	.0108	.0107	$10\bar{2}$
9.2	20	200	9.2	<10	200	9.148	5	.0120	.0120	200
8.5	20	002	8.4	<10	002	8.354	4	.0143	.0142	002
						6.942	2	.0208	.0207	$30\bar{1}$
						6.486	3	.0238	.0237	$1\bar{2}2$
6.35	30	$10\bar{3}$	6.32	10	$10\bar{3}$	6.285	11	.0253	.0253	$10\bar{3}$
5.60	10	003	5.60	<10	003	5.590	4	.0320	.0320	003
5.30	10	$40\bar{2}$	5.29	<10	$40\bar{2}$	5.273	6	.0360	.0361	$40\bar{2}$
5.15	60	$40\bar{1}$	5.13	20	$40\bar{1}$	5.116	48	.0382	.0384	$40\bar{1}$
			4.74	<10	103	4.734	4	.0446	.0447	103
4.63	50	$10\bar{4}$	4.63	20	$10\bar{4}$	4.616	36	.0469	.0469	$10\bar{4}$
						3.852	6	.0674	.0672	$30\bar{5}$
3.83	20	$20\bar{5}$ 010	3.83	<10	010	3.821	6	.0685	.0684 .0684	010 $20\bar{5}$
3.75	100	110	3.75	70	$40\bar{5}$				.0714	110
			3.74	50	110	3.737	100	.0716	.0717	111
									.0719	$40\bar{5}$
3.65	100	$10\bar{5}$	3.65	100	$10\bar{5}$	3.636	100	.0756	.0757	$10\bar{5}$
3.59	10	111	3.56	<10	111	3.577	4	.0782	.0782	111
3.56	20	$11\bar{2}$		0	$11\bar{2}$	3.553	4	.0792	.0791	$11\bar{2}$
						3.515	4	.0809	.0804	210
									.0812	$60\bar{3}$
									.0816	$21\bar{2}$
3.49	100	$60\bar{3}$ $60\bar{2}$ 012	3.49	50	$21\bar{2}$	3.483	100	.0824	.0826 .0826	$50\bar{5}$ 012
									.0829	$60\bar{2}$
3.41	10	$60\bar{4}$	3.41	<10	$60\bar{4}$	3.406	4	.0862	.0867	$60\bar{4}$
				0	402	3.383	4	.0874	.0879	402
3.36	60	$005/31\bar{1}$	3.36	10	005	3.351	28	.0891	.0889	005
									.0891	$31\bar{1}$
3.32	20	$60\bar{1}$	3.32	<10	211	3.316	5	.0909	.0904	211
			3.28	<10	$21\bar{3}$				.0917	$60\bar{1}$
									.0929	$21\bar{3}$
3.27	20	$11\bar{3}$		0	$11\bar{3}$	3.264	4	.0939	.0937	$11\bar{3}$
						3.247	4	.0949	.0948	204
3.17	40	013	3.17	<10	$20\bar{6}$	3.153	11	.1006	.1004	013
									.1045	$41\bar{2}$
3.09	20	$50\bar{6}$	3.09	<10	$41\bar{2}$	3.078	6	.1055	.1055	$50\bar{6}$
3.00	30	$10\bar{6}$ 214	3.01	<10	$10\bar{6}$	2.994	7	.1116	.1113 .1116	$21\bar{4}$ $10\bar{6}$
2.95	10	$11\bar{4}$							.1153	$11\bar{4}$
2.84	90	$51\bar{2}$ 014	2.84	10	$51\bar{2}$	2.832	36	.1247	.1249	$51\bar{2}$
2.82	10	$51\bar{3}$	2.83	10	$70\bar{1}$	2.826	38	.1252	.1253	014
									.1265	513
									.1273	$70\bar{1}$
2.77	80	$51\bar{1}$	2.78	20	$51\bar{1}$	2.771	31	.1303	.1305	$51\bar{1}$
2.73	10	$51\bar{4}$							.1306	601
2.70	80	$21\bar{5}$	2.71	20	$21\bar{5}$	2.701	34	.1371	.1352	514
2.70	10	$70\bar{6}$							.1369	$21\bar{5}$
									.1383	706
2.67	10	$41\bar{5}$	2.677	<10	$41\bar{5}$	2.668	3	.1405	.1403	$41\bar{5}$
2.65	20	510		0	$20\bar{7}$	2.644	4	.1431	.1408	$20\bar{7}$
									.1431	510
2.63	20	$80\bar{3}$	2.635	<10	$11\bar{5}$	2.628	5	.1448	.1441	$11\bar{5}$
									.1444	804
2.58	10	$51\bar{5}$ 612							.1454	$80\bar{3}$
		$80\bar{2}$							.1510	$51\bar{5}$
2.54	70	614	2.549	10	$10\bar{7}$	2.543	36	.1546	.1513	$61\bar{2}$
		503							.1536	$80\bar{2}$
									.1545	$10\bar{7}$
									.1551	614
2.53	10	412	2.537	<10	503				.1553	503
				0	404				.1564	412
				0	412				.1565	313
2.53	30	015	2.529	<10	313	2.523	5	.1571	.1565	404
									.1573	015
2.49	50	$70\bar{7}$	2.496	10	$80\bar{6}$	2.491	26	.1612	.1619	$70\bar{7}$
2.48	30	214	2.483	<10	511	2.478	8	.1629	.1629	511
									.1632	214
2.45	20	$41\bar{6}$	2.457	<10	$61\bar{5}$	2.452	5	.1664	.1637	$80\bar{6}$
									.1665	416
									.1688	801

See footnotes at end of table.

TABLE 1. *X-ray powder diffraction data for high temperature* Nb_2O_5—Continued

Magneli and Lagergren [9]			Holzberg et al. [8]			Present work CuK_{α_1} radiation				
d_{obs}	I/I_0	hkl[a]	d_{obs}	I/I_0	hkl[b]	d	I/I_0	$1/d^2_{obs}$	$1/d^2_{calc}$[c]	hkl[d]
									0.1837	712
									.1840	807
									.1851	905
2.339	20	712	2.340	<10	903				.1865	903
		616							.1871	413
2.315	80	413	2.319	10	208	2.314	29	0.1868	.1873	616
		208							.1877	208
2.282	10	708							.1925	708
									.2060	702
2.210	20	702							.2121	907
2.175	10	907	2.181	<10	814				.2128	814
									.2139	813
2.162	20	617		0	813				.2141	617
				<10	513				.2237	513
2.111	20	414	2.112	0	414	2.111	4	0.2244	.2249	414
									.2316	207
									.2321	816
2.075	80	10, 0, 3	2.079	10	207	2.076	38	.2321	.2324	10, 0, 6
									.2328	315
									.2336	10, 0, 3
			2.041	20	10, 0, 7					
				0	809					
									.2410	711
2.036	80	209	2.037	10	604	2.037	34	.2411	.2411	518
									.2416	209
									.2422	604
									.2459	809
									.2462	10, 0, 7
									.2524	817
1.985	10	817							.2683	117
1.931	10	6, 0, 10	1.934	<10	117				.2687	6, 0, 10
		118							.2730	118
		020							.2736	020
1.912	100	901	1.915	20	712	1.912	29	.2736	.2738	712
		11, 0, 6							.2744	901
									.2747	11, 0, 6
									.2827	221
									.2853	3, 0, 10
1.872	30	11, 0, 7	1.876	<10	221	1.873	5	.2852	.2856	220
		220							.2862	11, 0, 7
									.2879	022
1.865	10	022							.2880	009
		009							.2890	619
				<10	10, 1, 4				.2891	811
1.855	20	208	1.857	0	208	1.856	3	.2903	.2914	208
									.2945	10, 1, 4
									.2958	319
1.840	10	319							.2981	223
1.830	10	223							.2989	123
		123								
									.3005	320
		2, 0, 10							.3020	10, 1, 3
1.820	60	11, 0, 8	1.822	10	320	1.819	20	.3020	.3027	2, 0, 10
									.3039	11, 0, 8
									.3120	421
			1.793	10	902	1.789	16	.3124	.3127	407
									.3128	222
									.3145	902
			1.762	<10	10, 0, 10	1.765	5	.3211	.3214	420
			1.744	10	119	1.742	23	.3295	.3294	11, 0, 1
									.3302	119
									.3303	10, 0, 10
									.3355	4, 0, 11
						1.727	25	.3353	.3355	10, 1, 8
									.3357	521
									.3421	225
						1.709	10	.3424	.3422	4, 1, 10
									.3483	520
			1.694	10	520	1.692	20	.3493	.3493	125
			1.685	10	3, 1, 10	1.683	51	.3529	.3522	606
						1.627	8	.3776	.3537	3, 1, 10
										10, 0, 2
			1.590	<10	522	1.592	27	.3945	.3946	1, 1, 10
									.3949	522
			1.584	10	10, 1, 1	1.582	20	.3994	.3997	11, 0, 11
						1.579	18	.4012	.4009	721
									.4016	026
									.4031	10, 1, 1
			1.557	10	904	1.556	22	.4130	.4138	13, 0, 9
									.4140	12, 1, 3
									.4155	904

[a] The parameters upon which these *hkl* values are based are $a=21.50$ A, $b=3.825$ A, $c=20.60$A, $\beta=121°\ 45'$.
[b] The parameters upon which these *hkl* values are based are $a=21.34$ A, $b=3.816$ A, $c=19.47$ A, $\beta=120°\ 20'$.
[c] Only those values are listed which were either found as peaks in the present study or reported as peaks by previous workers.
[d] The parameters upon which these *hkl* values are based are $a=21.08$ A, $b=3.823$ A, $c=19.33$ A, $\beta=119°\ 48'$.

It can easily be seen that the larger "pseudo-cell" is related to the smaller "simplest-cell" by a doubling of the hexagonal a axis. For the "simplest-cell" $a_H=6.04$ A, $c_H=15.394$ A and for the "pseudo-cell" $a_H=12.093$ A, $c_H=15.394$ A. The pattern was indexed by Francombe using hexagonal hkl values for the larger cell. However, a simple examination of this indexing reveals that many of the hkl values used are not allowed by a rhombohedral cell, where $h-k+l=3n$. Furthermore, the observed versus calculated d spacings do not fit for many of the lines. The same observations are true for the "simplest-cell."

Cook [15] has given the rhombohedral unit cell of the low-temperature form of $PbO{\cdot}Nb_2O_5$ as $a_R=7.168$ A and $\alpha_R=93°\ 52'$. These parameters correspond to a hexagonal unit cell of $a=10.473$ A and $c=11.549$ A. This cell is related to Francombe's "simplest-cell" by a multiplication and rotation of the unit-cell parameters of the hexagonal cell:

$$a_H\ (\text{Cook})=\sqrt{3}\ a_H\ (\text{Francombe}),$$
$$c_H\ (\text{Cook})=3/4\ c_H\ (\text{Francombe}).$$

An X-ray powder pattern of the rhombohedral form of $PbO{\cdot}Nb_2O_5$, indexed on the basis of the cell suggested by Cook, is shown in table 2. The unit-cell parameters of this material are found to be $a_R=7.184$ A, $\alpha_R=93°\ 55'$; $a_H=10.510$ A, $c_H=11.562$ A.

b. Metastable Orthorhombic Ferroelectric Modification

The orthorhombic modification was the first form of $PbO{\cdot}Nb_2O_5$ to be reported. It was discovered to be ferroelectric by G. Goodman [1] who reported an orthorhombic unit cell having the approximate dimensions $a=25$ A, $b=25$ A, $c=7.0$ A. Francombe [2] found that the ferroelectric form only occurred when the specimen had been heated above the phase transformation temperature of 1,200° to 1,250° C. He reported this form to be orthorhombic with $a=17.51$ A, $b=17.81$ A, $c=7.73$ A. In a previous publication arising from the present work [14] the X-ray powder diffraction pattern of the ferroelectric modification of $PbO{\cdot}Nb_2O_5$ was indexed on the basis of an orthorhombic unit cell with $a=17.63$ A, $b=17.93$ A, $c=3.868$ A. Long film exposures using single-crystal techniques have shown that the true unit cell actually has a c axis value of twice that given [15]. This larger value does not show up in a Geiger counter tracing of the powder diffraction pattern. It has been shown [14] that the ferroelectric modification is only metastable, reverting to the rhombohedral form if heated several times from room temperature to 700° C. It, therefore, has no field of stability in the binary system $PbO-Nb_2O_5$.

c. High-Temperature Tetragonal Modification

Goodman [1] added small amounts of ZrO_2 and/or TiO_2 to his materials in order to obtain dense ceramics. Roth [14] has shown that the addition of such impurities has the effect of producing the orthorhombic structure in a form apparently stable at room temperature regardless of further heat treatments in laboratory time. A solid solution, of $PbO{\cdot}Nb_2O_5$ plus 2 weight percent of $ZrO_2{\cdot}TiO_2$, was examined by high-temperature X-rays at 600° C, above the ferroelectric Curie point. The resulting pattern could be indexed on the basis of a tetragonal unit cell with $a=12.56$ A and $c=3.925$ A [14]. It is still not known whether the c axis should be doubled for the true tetragonal cell.

High-termperature X-ray patterns made in this laboratory, indicate that pure $PbO{\cdot}Nb_2O_5$ has tetragonal symmetry, as a stable modification, from the temperature of the high-low phase transformation to the melting point. If the high-temperature modification is cooled quickly below the transformation point, it will maintain the tetragonal structure in a metastable condition. When it reaches the Curie point, reported as 590° C by Goodman [1], it transforms metastably and reversibly to the orthorhombic ferroelectric modification.

TABLE 2. *X-ray diffraction powder data for low temperature, rhombohedral* $PbNb_2O_6$ (CuK_{α_1} *Radiation*)

d	I/I_0	$1/d^2_{obs}$	$1/d^2_{calc}$ [a]	Rhombohedral	Hexagonal
				hkl	hkl
7.184	5	0.0194	0.0196	010	011
5.270	13	.0360	.0363	01$\bar{1}$	110
4.889	3	.0418	.0420	110	102
4.231	7	.0559	.0558	11$\bar{1}$	201
3.109	100	.1035	.1036	120	113
3.034	100	.1086	.1088	11$\bar{2}$/12$\bar{1}$	300
2.957	10	.1144	.1146	121	212
2.626	11	.1450	.1451	022	220
2.383	7	.1760	.1761	030/22$\bar{1}$	033
2.170	69	.2123	.2124	131	223
2.116	6	.2233	.2234	222	402
2.061	5	.2353	.2354	131	025
2.054	10	.2371	.2372	032	231
1.9840	48	.2541	.2539	123/132	410
1.9270	9	.2693	.2693	222	006
1.9012	5	.2767	.2769	23$\bar{1}$	314
1.8093	10	.3055	.3056	231	116
1.7964	8	.3099	.3097	223	501
1.7640	100	.3214	.3212	04$\bar{1}$/23$\bar{2}$	143
1.7502	58	.3265	.3264	033	330
1.6477	4	.3683	.3685	04$\bar{2}$	242
1.6263	40	.3781	.3781	141/330	036
1.5530	7	.4146	.4144	240	226
			.4149	331	207
1.5156	22	.4353	.4353	22$\bar{4}$/24$\bar{2}$	600
1.3826	10	.5231	.5232	150/341	146
1.3620	18	.5391	.5389	05$\bar{2}$/24$\bar{3}$	253
1.3483	20	.5501	.5498	152	162
1.3360	5	.5603	.5600	151	047
1.3336	5	.5623	.5618	34$\bar{2}$	515
1.3126	13	.5804	.5803	044	440
1.2955	22	.5958	.5957	25$\bar{1}$	336
1.2542	6	.6357	.6359	251	138
1.2481	5	.6420	.6422	342	119
1.2425	4	.6478	.6477	153	443
1.1912	11	.7047	.7046	060/442	066
1.1613	7	.7415	.7414	160	157
1.1536	6	.7514	.7510	351	229
1.1493	100	.7571	.7565	34$\bar{4}$/16$\bar{2}$	713
1.1421	8	.7666	.7674	154	542
1.1314	4	.7812	.7810	161	058
			.7813	335	801
1.1067	6	.8165	.8157	353	625
1.0958	5	.8328	.8327	352	1, 2, 10
1.0846	12	.8501	.8496	262	446
1.0782	28	.8602	.8598	261/450	149

[a] These values are based on the unit-cell parameters $a_H=10.501$ A, $c_H=11.562$ A, $a_R=7.184$ A, $\alpha_R=93°\ 55'$.

d. Pyrochlore-Type Modification

Cook [15] has claimed that another low-temperature form of $PbO{\cdot}Nb_2O_5$ exists below 700° C and that it "appears to be a pyrochlore structure previously unreported for lead niobate of this formula." Examination of the X-ray pattern of $PbO{\cdot}Nb_2O_5$ heated at 550° C for 16 hr as well as that of a specimen supplied by Cook, showed that the pyrochlore-type phase reported actually was $3PbO{\cdot}2Nb_2O_5$, and that rhombohedral $PbO{\cdot}Nb_2O_5$ and free Nb_2O_5 also were present. It can therefore be concluded that $PbO{\cdot}Nb_2O_5$ does not form a pyrochlore-type structure under any conditions.

3.4. Compound $2PbO{\cdot}Nb_2O_5$

The compound $2PbO{\cdot}Nb_2O_5$ has been studied by Cook and Jaffe [3,4], Shirane and Pepinsky [17], Hulm [18], and Jona, Shirane, and Pepinsky [19]. Cook and Jaffe [3] list the compound $2PbO{\cdot}Nb_2O_5$ as rhombohedral with $a=5.285$ A and $\alpha=89°\ 15'$. They later [4] imply that the a axis should be doubled, thus suggesting a rhombohedral distortion of the pyrochlore-type structure. Jona, Shirane, and Pepinsky [19] give values of $a=10.674$ A, $\alpha=88°\ 50'$. The values obtained in the present study are $a=10.676$ A, $\alpha=88°\ 44'$, and the indexed X-ray diffraction pattern is given in table 3. Shirane and Pepinsky [17] and Hulm [18] have shown a dielectric anomaly in $2PbO{\cdot}Nb_2O_5$ at about 14° K, indicating a phase transformation, but nothing is known of the structure of this phase.

3.5. Compound $3PbO{\cdot}2Nb_2O_5$

Cook and Jaffe [4] reported the observation of a cubic pyrochlore-type phase at approximately "the composition $Pb_{1.5}Nb_2O_{6.5}$" but did not definitely call it a compound. They observed a unit-cell parameter for this composition of 10.561 A. In the present study this phase has been identified as a compound with little or no solid solution, of the composition $3PbO{\cdot}2Nb_2O_5$. It has been found to melt incongruently at 1,233° C to liquid plus $PbO{\cdot}Nb_2O_5$.

3.6. Compound $5PbO{\cdot}2Nb_2O_5$

This compound has not been previously reported. It was discovered in the present work by observing that compositions in the area containing a single-phase rhombohedral pyrochlore-type structure did not begin melting at temperatures to be expected from a simple solid-solution region. It was obvious that a new compound of approximately the ratio 5:2 had to be introduced in order to explain the melting-point data. This composition containing 71.43 mole percent of PbO is the high PbO end member of this solid-solution series. The composition containing 72 mole percent of PbO shows some of the compound $3PbO{\cdot}Nb_2O_5$. The compound $5PbO{\cdot}2Nb_2O_5$ apparently has the same symmetry as the 2:1 compound, probably rhombohedral. The 5:2 compound shows a larger distortion from the ideal cubic pyrochlore-type structure than does the compound $2PbO{\cdot}Nb_2O_5$. The parameters observed for the 5:2 compound are $a_R=10.709$ A; $\alpha_R=88°\ 14'$.

TABLE 3. *X-ray diffraction powder data for rhombohedral* $2PbO{\cdot}Nb_2O_5$ (CuKα_1 *radiation*)

d	I/I_0	I/I^2_{obs}	$1/d^2_{calc}$ [a]	Rhombohedral	Hexagonal
				hkl	hkl
7.10	3	0.0199	-------	-------	(b)
6.29	7	.0253	0.0252	111	003
3.543	4	.0796	.0791	030/22$\bar{1}$	303
3.393	3	.0869	.0867	130	124
3.142	65	.1013	.1009	222	006
3.056	100	.1071	.1069	22$\bar{2}$	402
2.667	100	.1406	.1405	040	044
2.438	3	.1683	.1657	33$\bar{1}$	405
			.1703	13$\bar{3}$	421
2.410	7	.1722	.1726	240	226
2.390	5	.1751	.1787	042	242
2.015	8	.2464	.2449	342	119
1.9064	39	.2751	.2750	440	408
1.8664	45	.2871	.2871	044	440
1.6305	27	.3762	.3759	26$\bar{2}$	0, 4, 10
1.6053	33	.3881	.3879	26$\bar{2}$	446
1.5935	18	.3938	.3940	2$\bar{6}$2	082
1.5744	7	.4034	.4034	444	0, 0, 12
1.5297	19	.4274	.4276	44$\bar{4}$	804
1.3333	9	.5625	.5621	080	088
1.2450	4	.6452	.6448	662	4, 0, 14
1.2282	7	.6629	.6629	66$\bar{2}$	8, 0, 10
1.2122	14	.6805	.6810	266	842
1.2028	9	.6912	.6905	480	4, 4, 12
1.1832	11	.7143	.7147	08$\bar{4}$	484
1.1092	3	.8128	.8129	48$\bar{4}$	0, 4, 16
1.0857	6	.8484	.8491	48$\bar{4}$	848
1.0781	4	.8604	.8612	448/48$\bar{4}$	12, 0, 0

[a] These values are based on the unit-cell parameters

$a_H=14.931$ A, $c_H=18.893$ A, $a_R=10.676$ A, $\alpha=88°\ 44'$.

[b] This peak does not fit the proposed rhombohedral structure, but it is reproducible and apparently indicates a lower symmetry for the true structure of $2PbO{\cdot}Nb_2O_5$. Such a peak also occurs in the patterns of the compound $5PbO{\cdot}2Nb_2O_5$ and the solid solutions between the two.

The composition of the 5:2 compound can be arrived at by analogy to the pyrochlore-type structure. The theoretical cubic pyrochlore-type structure contains 16 A ions, 16 B ions, and 56 negative ions. Of the negative ions, 48 occupy one set of equivalent positions and 8 ions occupy another. In the $PbO{\cdot}Nb_2O_5$ system a unique compound is formed at a ratio of 1½ Pb^{+2} ions to $2Nb^{+5}$ ions or $Pb_{1.5}Nb_2O_{6.5}$ ($Pb_{12}Nb_{16}O_{48}O_4$). On the high-PbO side of the pyrochlore-type formula a likely compound is one in which 8 oxygen ions are missing, those belonging to the 8-fold equivalent position. This type of compound would be $Pb_2Nb_{1.6}O_6$ ($Pb_{16}Nb_{12.8}O_{48}$) which has a $PbO{:}Nb_2O_5$ ratio of 5:2. This composition is observed to be the high-PbO end of the solid solution series.

3.7. Compound $3PbO{\cdot}Nb_2O_5$

The compound $3PbO{\cdot}Nb_2O_5$ has also not been previously reported. It has a distorted pyrochlore-type structure which resembles $2PbO{\cdot}Nb_2O_5$, except that the distortion is of a pseudo-tetragonal rather than a rhombohedral type. The face-centered tetragonal parameters for this phase are $a=10.658$ A. $c=10.824$ A. As can be seen in the X-ray pattern of table 4, there are some diffraction peaks which cannot be indexed on the basis of this face-centered cell, but do fit a primitive cell of the same dimen-

TABLE 4. *X-ray diffraction powder data for the compound* $3PbO \cdot Nb_2O_5$ (CuK_{α_1} *radiation*)

d	I/I_0	$1/d^2_{obs}$	$1/d^2_{calc}$ [a]	hkl
6.78	7	0.0217	--------	--------
6.18	16	.0262	0.0262	111
5.886	3	.0289	--------	--------
5.611	5	.0318	--------	--------
3.419	7	.0856	.0856	[b] 103
3.218	12	.0966	.0966	311
3.093	100	.1045	.1046	222
2.943	14	.1154	.1144	[b] 320
2.706	69	.1366	.1366	004
2.662	100	.1411	.1408	400
2.461	13	.1651	.1649	313
2.444	8	.1674	.1670	331
2.404	4	.1731	--------	--------
2.354	5	.1805	.1806	[b] 214
2.077	4	.2319	.2310	115
2.051	8	.2378	.2374	511
1.8989	100	.2773	.2774	404
1.8834	54	.2819	.2817	440
1.6268	58	.3779	.3777	226
1.6091	100	.3862	.3863	622
1.5461	41	.4183	.4183	444
1.3530	8	.5463	.5463	008
1.3323	15	.5634	.5634	800
1.2317	37	.6592	.6594	626
1.2247	13	.6667	.6679	662
1.2224	13	.6692		
1.2066	17	.6869	.6871	408
1.1953	17	.6999	.6999	804
1.1923	18	.7034	.7042	840
1.0991	11	.8278	.8280	448
1.0912	16	.8398	.8408	844
1.0406	7	.9235	.9240	2, 2, 10
1.0313	7	.9402	.9411	666
1.0262	16	.9496	.9496	10, 2, 2

[a] These values are based on a tetragonal unit cell with $a=10.658$ A, $c=10.824$ A.
[b] These peaks are not allowed by a face-centered cell.

TABLE 5. *X-ray diffraction powder data for the compound* $PbO \cdot 2Nb_2O_5$ (CuK_{α_1} *radiation*)

d	I/I_0	hkl [a]	d	I/I_0	hkl [a]
8.84	7	110	2.441	9	041
6.24	15	020	2.313	4	250
5.576	15	120	2.139	7	------
3.948	32	001	2.126	9	350
3.857	6	--------	2.073	6	060
3.601	5	--------	1.996	5	260
3.528	8	--------	1.972	35	002
3.455	14	230	1.858	7	------
3.333	16	021	1.850	5	------
3.218	55	121	1.757	4	451
3.109	5	040	1.739	4	------
3.067	8	--------	1.711	4	------
3.020	100	140	1.681	8	------
2.942	32	330/221	1.649	16	142
2.861	5	--------	1.637	6	------
2.786	60	240/131	1.604	15	242
2.627	4	--------	1.508	4	------
2.596	23	231	1.450	5	------
2.520	4	--------	1.312	7	------

[a] The hkl values are given by analogy to the tetragonal structure of high temperature $PbO \cdot Nb_2O_5$. This is only a pseudo-cell, as there are many peaks which cannot be indexed on this basis. The pseudo-tetragonal cell has unit-cell parameters of $a=12.44$ A, $c=3.94$ A.

sions. However, there are still other d-spacings which cannot be indexed at all on this tetragonal cell. Although the pattern is very strongly pseudo-tetragonal, it must be concluded that the true symmetry is still unknown.

3.8. Compound $PbO \cdot 2Nb_2O_5$

The compound $PbO \cdot 2Nb_2O_5$ has not been previously reported. This new compound can easily be observed by X-ray diffraction studies of specimens of the 1:2 composition, or of compositions between 1:1 and 1:2, heated in the range in which the rhombohedral form of $PbO \cdot Nb_2O_5$ would be expected. It was found in the present study to have an X-ray pattern very similar to the orthorhombic and tetragonal forms of $PbO \cdot Nb_2O_5$. However, there are some lines in the pattern that cannot be indexed on either basis, as shown in table 5. This compound is isostructural with $BaO \cdot 2Nb_2O_5$ which also has these extra lines. It must be concluded that the true symmetry of $PbO \cdot 2Nb_2O_5$ is, as yet, unknown.

4. Discussion of Phase Equilibria

The phase-equilibrium diagram of the binary system PbO–Nb_2O_5 is shown in figure 1. The data from which this diagram has been constructed are given in table 6. The system contains four congruently melting compounds $5PbO \cdot 2Nb_2O_5$, $2PbO \cdot Nb_2O_5$, $PbO \cdot Nb_2O_5$, and $PbO \cdot 2Nb_2O_5$; and two incongruently melting compounds $3PbO \cdot Nb_2O_5$ and $3PbO \cdot 2Nb_2O_5$.

PbO has been accepted as melting at 883 $\pm 5°$ C [20]. There is an eutectic between PbO and $3PbO \cdot Nb_2O_5$ at approximately 94 mole percent of PbO and 835° C. The eutectic temperature was located by X-ray diffraction analyses of quenched specimens from sealed Pt tubes (see section 5). When a specimen in the two-phase region was quenched from below the solidus, yellow PbO and $3PbO \cdot Nb_2O_5$ were found to coexist. Changes in d-spacings of the X-ray patterns indicate that a small amount of solid solution, less than 2 mole percent, probably exists in the yellow PbO phase.

The compound $3PbO \cdot Nb_2O_5$ was found to melt incongruently to $5PbO \cdot 2Nb_2O_5$ plus liquid at 985° C. Specimens containing 75 mole percent of PbO, in a sealed Pt tube, quenched from below this temperature showed only the compound $3PbO \cdot Nb_2O_5$. Specimens of the same composition quenched from just above this temperature showed some of the compound $5PbO \cdot 2Nb_2O_5$. The compound $5PbO \cdot 2Nb_2O_5$ is essentially isostructural with $2PbO \cdot Nb_2O_5$, and there is apparently complete solid solution between the two. The compound $5PbO \cdot 2Nb_2O_5$ appears to melt congruently at approximately 1,220° C. There may be a very small eutectic or minimum in the solid-solution area close to the 5-2 compound or this compound might actually melt incongruently; however, any such discrepancies from the situation shown in figure 1 are so small as to be undetectable with the present experimental equipment.

The compound $2PbO \cdot Nb_2O_5$ was observed to melt congruently at about 1,233° C. Specimens sealed in a Pt tube and quenched from below this temperature showed no sign of melting. Above this temperature, the specimen appeared to be completely melted.

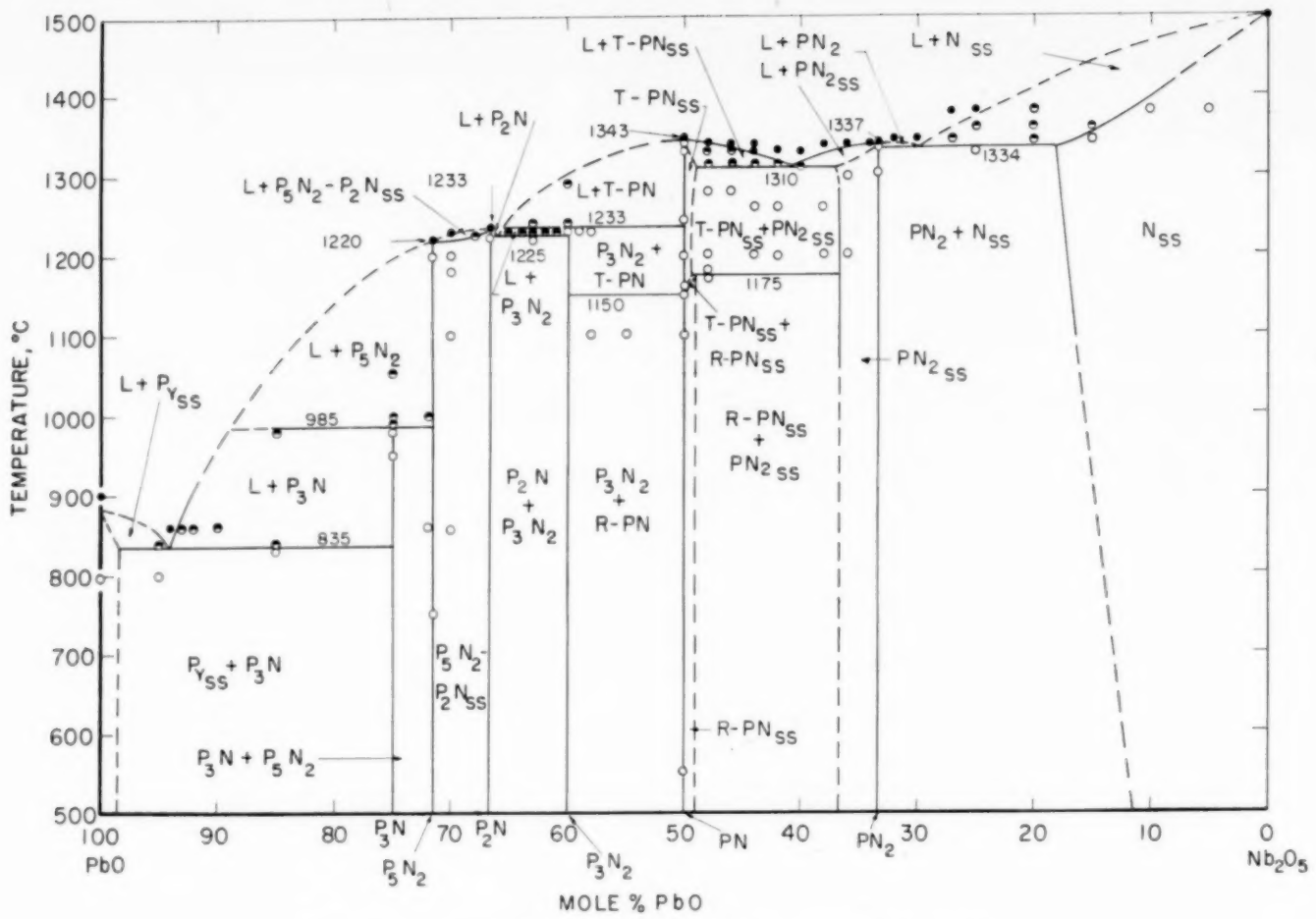

FIGURE 1. *Phase equilibrium diagram for the system* PbO—Nb_2O_5.

P_Y—yellow PbO, orthorhombic; P_3N—$3PbO{\cdot}Nb_2O_5$; P_5N_2—$5PbO{\cdot}2Nb_2O_5$; P_2N—$2PbO{\cdot}Nb_2O_5$; P_3N_2—$3PbO{\cdot}2Nb_2O_5$; T-PN—tetragonal $PbO{\cdot}Nb_2O_5$; R-PN—rhombohedral $PbO{\cdot}Nb_2O_5$; PN_2—$PbO{\cdot}2Nb_2O_5$; N—Nb_2O_5; SS—solid solution; ○—no melting; ◓—partial melting; ●—completely melted.

No phase other than that of $2PbO{\cdot}Nb_2O_5$ was observed in the X-ray pattern of a quenched specimen of the melted material, thus strongly indicating congruent melting.

Compositions between $2PbO{\cdot}Nb_2O_5$ and $PbO{\cdot}Nb_2O_5$ give conflicting data when examined as quenched specimens from sealed tubes and as ceramic pellets heated in air. Cook and Jaffe [4] observed a single-phase cubic pyrochlore-type structure at a composition corresponding to "$Pb_{1.5}Nb_2O_{6.5}$" or 60 mole percent of PbO. This observation was confirmed in the present study for both air and sealed-tube techniques. However, Cook [21] has stated that in "a closely spaced series of compositions between $Pb_2Nb_2O_7$ and $Pb_{1.5}Nb_2O_{6.5}$ . . . extra lines of the rhombohedral splitting do not draw closer to the main lines of the pattern, as you would expect. They just fade out." A similar phenomena was observed in the present study for specimens prepared at 1-mole-percent intervals between 65 and 60 mole percent of PbO, when heated in covered Pt crucibles.

When these specimens were quenched in sealed Pt tubes a clear picture of a two-phase region with little or no solid solution was observed for temperatures of 1,220° C or below. At 1,230° C the cubic $3PbO{\cdot}2Nb_2O_5$ phase greatly predominated throughout all the specimens from 65 to 61 mole percent of PbO. The rhombohedral $2PbO{\cdot}Nb_2O_5$ phase was found to coat the walls of the Pt tube and was difficult to recover, thus indicating that this phase had been in the vapor state and that these specimens had been above the eutectic temperature. The eutectic composition could not be located exactly but is probably close to 66 percent of PbO. The eutectic temperature was thus located at 1,225 ±5° C. In the sealed tube, the composition containing 60 mole percent of PbO was found to melt incongruently at 1,233° C, forming some $PbO{\cdot}Nb_2O_5$. Compositions of 59 and 58 mole percent of PbO contained both cubic $3PbO{\cdot}2Nb_2O_5$ and $PbO{\cdot}Nb_2O_5$ when quenched in the sealed tube from below the solidus. Therefore, a compound of the ratio $3PbO{\cdot}2Nb_2O_5$ has been fully established.

TABLE 6. *Experimental data for compositions in the binary system* $PbO–Nb_2O_5$

Composition		Experimental procedure		Heat treatment		Results	
PbO	Nb_2O_5	Air	Sealed Pt tube, quenched	Temperature	Time	Physical observation	X-Ray diffraction analyses [d]
mol %	*mol %*			*° C*	*hr*		
100	0	X		470	30	Bright red	Pb_3O_4.
			X	471	65	Yellow	Orth.–PbO.
			X	487	16	Yellow	Do.
			X	798	1.5	Yellow	Do.
			X	900	0.16	Yellow, melted	Do.
95	5	X		786	1		Orth·PbO+3PbO·Nb_2O_5.
			X	471	65	Orange-yellow	Do.
			X	487	16	Orange-yellow	Do.
			X	798	1.5		Do.
			X	832	0.11	Yellow with red spots, partially melted	Orth·PbO+tet·PbO_{ss}.
94	6		X	860	.05	Dark reddish brown, melted	Tet·PbO_{ss}+trace of 3 PbO·Nb_2O_5 and orth·PbO.
			[c] X	824	16.00	Black-metallic luster, grinds to yellowish brown.	Orth·PbO+3 PbO·Nb_2O_5 (no tet·PbO_{ss}).
93	7		X	860	0.03	Reddish brown, melted	Tet·PbO_{ss}+3PbO·Nb_2O_5.
92	8		X	860	.03	Reddish brown, melted	Do.
90	10	X		750	1		Orth. PbO+3PbO·Nb_2O_5.
			X	860	.05	Mostly melted, vesicular	Tet. PbO_{ss}+3PbO·Nb_2O_5.
85	15	X		786	1		3PbO·Nb_2O_5+orth.PbO.
			X	830	.08	Not melted	Do.
			X	840	.08	Some melting	Tet·Pbo_{ss}+3PbO·Nb_2O_5.
			X	978	.08	Mostly melted, vesicular	Do.
80	20	X		786	1		3PbO·Nb_2O_5+orth. PbO.
		X		753	1		3PbO·Nb_2O_5.
		X		870	1		Do.
		X		900	1		Do.
		X		920	1	Lost weight	3PbO·Nb_2O_5+5PbO·2Nb_2O_5.
		X		950	1	Lost weight	Do.
75	25	X		1,008	1	Lost weight	5PbO·2Nb_2O_5.
			X	951	0.25	No melting	3PbO·Nb_2O_5.
			X	980	.16	No melting	Do.
			X	990	.16	Melting (?)	3PbO·Nb_2O_5+5PbO·2Nb_2O_5+tet. PbO_{ss}.
			X	1,000	.16	Some melting	5PbO·2Nb_2O_5+tet. PbO_{ss}.
			X	1,053	.16	Some melting	Do.
72	28		X	860	1.5		5PbO·2Nb_2O_5+3PbO·Nb_2O_5.
			X	1,000	0.33	Some melting (?)	5PbO·2Nb_2O_5+tet. PbO_{ss}.
			X	1,225	.08	Some melting (?)	
71.4285 (5:2)	28.5715		X	1,200	.08	No melting	5PbO·2Nb_2O_5.
			X	1,220	.08	Melted	5PbO·2Nb_2O_5+2PbO·Nb_2O5_{ss}+tet. PbO_{ss}.
			X	1,230	.02	Completely melted	
		X		753	1		3PbO·Nb_2O_5+5PbO·2Nb_2O_5−2PbO·Nb_2O_{5ss}.
		X		1,100	1	Lost weight	5PbO·2Nb_2O_5−2PbO·Nb_2O_{5ss}.
70	30		X	747	64		Do.
			X	856	0.5		Do.
			X	1,100	.08	No melting	Do.
			X	1,180	.16	No melting	Do.
			X	1,230	.08	No melting	
			X	1,250	.08	Melted	5PbO·2Nb_2O_5−2PbO·Nb_2O_{5ss}+tet. PbO_{ss}.
68	32		X	860	1.5		5PbO·2Nb_2O_5−2PbO·Nb_2O_{5ss}.
			X	1,225	0.02	Considerable melting	5PbO·2Nb_2O_5−2PbO·Nb_2O_{5ss}+tet. PbO_{ss}.
		X		1,075	1		2PbO·Nb_2O_5.
66.67	33.33		X	1,225	0.25	Not melted	Do.
			X	1,230	.16	....do	Do.
			X	1,235	.25	Melted	Do.
			X	1,247	.16	....do	Do.
			X	1,260	.16	....do	Do.
65	35	X		1,100	1		3PbO·2Nb_2O_5+2PbO·Nb_2O_5.
		X		1,100	1		[e] 2PbO·Nb_2O_5+3PbO·2Nb_2O_5.
			X	1,230	0.5	Some melting	2PbO·Nb_2O_5+3PbO·2Nb_2O_5.
64	36	X		1,100	1		3PbO·2Nb_2O_5+2PbO·Nb_2O_5.
			X	1,230	0.25	Some melting	Do.
63	37	X		1,100	1		Do.
			X	1,220	1.5	No melting	2PbO·Nb_2O_5+3PbO·2Nb_2O_5.
			X	1,230	0.16	Melting (?)	Do.
			X	1,240	.08	Some melting	3PbO·2Nb_2O_5+2PbO·Nb_2O_5.
62	38	X		1,100	1		Do.
			X	1,230	0.5	Some melting	Do.
61	39	X		1,100	1		Do.
			X	1,230	0.16	Some melting (?)	Do.
60	40	X		1,100	1		3PbO·2Nb_2O_5.
			X	1,225	0.25	No melting	Do.
			X	1,235	.25	Some melting	3PbO·2Nb_2O_5+orth. PbO·Nb_2O_5.
			X	1,285	0.08	Mostly melted	Do.
59	41	X		1,100	1		3PbO·2Nb_2O_5.
			X	1,230	0.11	No melting	3PbO·2Nb_2O_5+PbO·Nb_2O_5.
58	42	X		1,100	1		3PbO·2Nb_2O_5.
			X	1,230	0.11	No melting	3PbO·2Nb_2O_5+orth. PbO·Nb_2O_5.
56.5	43.5	X		1,259	1		3PbO·2Nb_2O_5− rhom·PbO·Nb_2O_5.
55	45	X		1,100	1		Do.
53.5	46.5	X		1,259	1		Rhom· PbO·Nb_2O_5+3PbO·2Nb_2O_5.
52	48	X		1,299	1		Orth. PbO·Nb_2O_5+3PbO·2Nb_2O_5.

TABLE 6. *Experimental data for compositions in the binary system* PbO–Nb_2O_5—Continued

Composition		Experimental procedure		Heat treatment		Results	
PbO	Nb_2O_5	Air	Sealed Pt tube, quenched	Temperature	Time	Physical observation	X-Ray diffraction analyses [d]
mol %	*mol %*			*°C*	*hr*		
		X	------	550	16	Not completely reacted	$3PbO{\cdot}2Nb_2O_5$+rhom. $PbO{\cdot}Nb_2O_5$+mon·Nb_2O_5.
		X	------	800	0.5	Completely reacted	Rhom. $PbO{\cdot}Nb_2O_5$.
		X	------	1,200	.5	------	Do.
		X	------	1,300	.5	------	Rhom. $PbO{\cdot}Nb_2O_5$+crth. $PbO{\cdot}Nb_2O_5$.
		X	------	1,350	.5	Melted	Orth. $PbO{\cdot}Nb_2O_5$.
		------	X	1,150	2	------	Rhom. $PbO{\cdot}Nb_2O_5$.
		------	X	1,150	24	------	Rhom. $PbO{\cdot}Nb_2O_5$+orth. $PbO{\cdot}Nb_2O_5$.
		------	X	1,160	2	------	Do.
50	50	------	X	1,200	0.5	------	Do.
		------	X	1,243	.25	------	Orth. $PbO{\cdot}Nb_2O_5$+rhom. $PbO{\cdot}Nb_2O_5$.
		------	X	1,329	.5	No melting	Orth. $PbO{\cdot}Nb_2O_5$.
		------	X	1,340	.25	No melting	Do.
		------	X	1,345	0	Melted	Do.
		[a] X	------	1,000	0	------	Rhom. $PbO{\cdot}Nb_2O_5$.
		[a] X	------	1,236	0	------	Rhom. $PbO{\cdot}Nb_2O_5$+tet. $PbO{\cdot}Nb_2O_5$.
		[a] X	------	1,287	0	------	Tet. $PbO{\cdot}Nb_2O_5$+rhom. $PbO{\cdot}Nb_2O_5$.
		[a] X	------	1,287	2	------	Tet. $PbO{\cdot}Nb_2O_5$.
		X	------	1,280	1	------	Orth. $PbO{\cdot}Nb_2O_{5ss}$+$PbO{\cdot}2Nb_2O_{5ss}$.
		[b] X	------	1,296	0.5	No melting	
		[b] X	------	1,314	.5	Some melting	
		[b] X	------	1,330	.5	Considerable melting	
48	52	[b] X	------	1,338	.5	Completely melted	
		------	X	1,170	.25	------	Rhom. $PbO{\cdot}Nb_2O_{5ss}$+$PbO{\cdot}2Nb_2O_{5ss}$.
		------	X	1,180	1	------	Rhom. $PbO{\cdot}Nb_2O_{5ss}$+orth. $PbO{\cdot}Nb_2O_{5ss}$+$PbO{\cdot}2Nb_2O_{5ss}$.
		------	X	1,200	0.25	------	Orth. $PbO{\cdot}Nb_2O_{5ss}$+$PbO{\cdot}2Nb_2O_{5ss}$.
		X	------	1,280	1	------	Do.
		[b] X	------	1,296	0.5	No melting	
46	54	[b] X	------	1,314	.5	Some melting	
		[b] X	------	1,330	.5	Almost completely melted	
		[b] X	------	1,338	.5	Completely melted	
		X	------	1,200	.16	------	Rhom. $PbO{\cdot}Nb_2O_{3ss}$+$PbO{\cdot}2Nb_2O_{5ss}$.
		X	------	1,265	0	------	Orth. $PbO{\cdot}Nb_2O_{5ss}$+$PbO{\cdot}2Nb_2O_{5ss}$.
44	56	[b] X	------	1,296	0.5	No melting	
		[b] X	------	1,314	.5	Considerable melting	
		[b] X	------	1,330	.5	Completely melted	
		X	------	1,200	1	------	Rhom $PbO{\cdot}Nb_2O_{3ss}$+$PbO{\cdot}2Nb_2O_{5ss}$.
		X	------	1,265	0	------	Orth. $PbO{\cdot}Nb_2O_{5ss}$+$PbO{\cdot}2Nb_2O_{5ss}$.
42	58	[b] X	------	1,296	0.5	No melting	
		[b] X	------	1,314	.5	Almost completely melted	
		[b] X	------	1,330	.5	Completely melted	
		X	------	1,265	0	------	$PbO{\cdot}2Nb_2O_{5ss}$+orth. $PbO{\cdot}Nb_2O_{5ss}$.
		[b] X	------	1,296	0.5	No melting	
40	60	[b] X	------	1,314	.5	Almost completely melted	
		[b] X	------	1,330	.5	Completely melted	
		------	X	1,310	.25	Partly melted	
		------	X	1,330	.25	Completely melted	
38	62	X	------	1,200	1	------	$PbO{\cdot}2Nb_2O_{5ss}$+rhom. $PbO{\cdot}Nb_2O_{5ss}$.
36	64	X	------	1,200	1	------	$PbO{\cdot}2Nb_2O_{5ss}$.
		X	------	1,299	1	------	Do.
34	66	X	------	1,304	1	------	Do.
		X	------	1,257	0	------	$PbO{\cdot}2Nb_2O_5$.
		X	------	1,301	48	------	Do.
		X	------	1,350	0.5	Melted	Do.
		[b] X	------	1,296	.5	No melting	
33.33	66.67	[b] X	------	1,314	.5	No melting	
		[b] X	------	1,330	.5	No melting	
		[b] X	------	1,338	.5	Completely melted	
		------	X	1,336	.25	No melting	$PbO{\cdot}2Nb_2O_5$.
		------	X	1,338	.16	Completely melted	Do.
32	68	X	------	1,304	1	------	$PbO{\cdot}2Nb_2O_5$+mon.Nb_2O_{5ss}.
		X	------	1,304	1	------	Do.
30	70	[b] X	------	1,340	0.5	Completely melted	
		------	X	1,338	.16	Completely melted	
27	73	[b] X	------	1,340	.5	Almost completely melted	
		[b] X	------	1,360	.5	Completely melted	
		X	------	1,265	0	------	$PbO{\cdot}2Nb_2O_5$+mon.Nb_2O_{5ss}.
		[b] X	------	1,296	0.5	No melting	
		[b] X	------	1,314	.5	No melting	
25	75	[b] X	------	1,330	.5	No melting	
		[b] X	------	1,338	.5	Considerable melting	
		[b] X	------	1,340	.5	Considerable melting	
		[b] X	------	1,360	.5	Almost completely melted	
		[b] X	------	1,380	.5	Completely melted	
		X	------	1,300	65	------	Mon.Nb_2O_{5ss}+$PbO{\cdot}2Nb_2O_5$.
20	80	[b] X	------	1,340	0.5	Some melting	
		[b] X	------	1,360	.5	Moderate melting	
		[b] X	------	1,380	.5	Considerable melting	
		X	------	1,300	65	------	Mon.Nb_2O_{5ss}+$PbO{\cdot}2Nb_2O_5$.
15	85	[b] X	------	1,340	0.5	No melting	
		[b] X	------	1,360	.5	Some melting	
		[b] X	------	1,380	.5	Moderate melting	
		X	------	1,257	0	------	Mon.Nb_2O_{5ss}+$PbO{\cdot}2Nb_2O_5$.
10	90	[b] X	------	1,340	0.5	No melting	
		[b] X	------	1,360	.5	No melting	
		[b] X	------	1,380	.5	No melting	
		X	------	770	1.0	------	Mon.Nb_2O_{5ss}.
		X	------	1,300	65	------	Do.
5	95	[b] X	------	1,340	0.5	No melting	
		[b] X	------	1,360	.5	No melting	
		[b] X	------	1,380	.5	No melting	

[a] This experiment was conducted in a high-temperature X-ray furnace.

[b] The specimens had been ground into the shape of four-sided-grooved pyramids.

[c] The melted specimen was sealed in another Pt tube and reheated to determine if equilibrium could be obtained from the nonequilibrium tetragonal PbO solid solution.

[d] The phases identified are given in the order of the amount present at room temperature. The phases are not necessarily those present at the temperature to which the specimen was heated: Mon.—monoclinic; orth.—orthorhombic; tet.—tetragonal; rhom.—rhombohedral; ss—solid solution.

[e] This X-ray pattern was made on the same specimen as preceding after grinding the surface of the specimen.

The compound $PbO{\cdot}Nb_2O_5$ was found to melt congruently at 1,343 $\pm 2°$ C by both the sealed-Pt-tube method and the grooved-pyramid method. However, the temperature of the rhombohedral-tetragonal phase transformation could not be arrived at by heating in air. It appears that this phase transformation is quite sluggish. High-temperature X-ray patterns in air show that several hours at 1,287° C are required to convert all of the low-temperature rhombohedral form to the high-temperature tetragonal form. A specimen heated at 1,200° C for 1 hr in air and examined at room temperature showed only the low-temperature form. However, the same material heated in a sealed Pt tube for 30 min at 1,200° C was converted in part to the high-temperature form. A 2-hr heat treatment as low as 1,160° C gave some of the high-temperature form while the same time at 1,150° C gave only low-temperature $PbO{\cdot}Nb_2O_5$. However, holding the 1:1 composition at 1,150° C for 24 hr did convert a small amount of the material to the high-temperature form. It seems that a maximum temperature of 1,150° C is as close to the transformation temperature as can be obtained in reasonable laboratory time.

$PbO{\cdot}Nb_2O_5$ will accept a small amount of Nb_2O_5 into solid solution as shown by significant changes in *d*-spacings of the X-ray patterns. However, the composition containing 48 mole percent of PbO has two phases, indicating that solid solution is less than 2 mole percent. This small amount of solid solution is enough to raise the temperature of the phase transformation from the rhombohedral to the tetragonal form by about 25° C, as shown by quenching experiments in sealed Pt tubes.

A eutectic exists between $PbO{\cdot}Nb_2O_5$ and $PbO{\cdot}2Nb_2O_5$ at about 41 mole percent of PbO and 1,310° C. This eutectic was found by the grooved-pyramid technique and checked with experiments using sealed Pt tubes. The compound $PbO{\cdot}2Nb_2O_5$ was found to melt, probably congruently, at 1,337° $\pm 2°$ C. $PbO{\cdot}2Nb_2O_5$ takes more than 2 but less than 4 mole percent of PbO into solid solution at the solidus temperature. This solid solution is retained on relatively slow cooling, as shown by X-ray patterns of specimens containing 36 and 38 mole percent of PbO.

Although $PbO{\cdot}2Nb_2O_5$ appears to melt sharply, no eutectic has been definitely located on the high Nb_2O_5 side. However, some melting-point data of the compositions containing 32 and 30 mole percent of PbO indicate a eutectic in this region. Both of these compositions appear completely melted, by the pyramid method, at 1,344° C. If the 1 : 2 compound melted incongruently, these specimens would be only partially melted at 1,344° C. A eutectic can, therefore, be placed at about 30 mole percent of PbO and 1,334 $\pm 4°$ C.

Nb_2O_5 is found to accept a little over 15 mole percent of PbO into solid solution at the eutectic temperature. As shown by X-ray diffraction this amount decreases to a little less than 10 mole percent at room temperature. The addition of PbO to Nb_2O_5 seems to lower the temperature of the phase transformation from the low to the high form of Nb_2O_5. The specimen containing 5 mole percent of PbO heated to 770° C for 1 hr contained only the high-temperature form of Nb_2O_5. This form was also found in the nonequilibrium assemblage of the 50 : 50 specimen at 550° C for 16 hr. No attempt has been made to locate accurately the temperature of this phase transformation in the presence of PbO. The low temperature form of Nb_2O_5 has not been indicated on the phase diagram of figure 1 as it seems likely that this polymorph is only metastable and has no true equilibrium position in the binary system. The melting point of Nb_2O_5 was accepted as 1,500 $\pm 10°$ C as found by Roth and Coughanour [22].

5. Occurrence of a Nonequilibrium Red PbO Solid Solution

When specimens of composition between pure PbO and the 2 : 1 compound are quenched from above the solidus, a phase similar to the tetragonal red PbO is observed in the X-ray patterns. This phase has an *a* parameter about the same as pure tetragonal PbO but a *c* parameter which is much larger. This *c* parameter is always approximately the same, regardless of the temperature or composition of the quenched specimen. It has a value of about 5.08 A as compared to the value of 5.023 A for pure PbO. Specimens containing 95 percent of PbO consisted only of yellow PbO and this red PbO solid solution, when quenched from above the solidus. When the composition is on the high-Nb_2O_5 side of the eutectic, the tetragonal solid solution occurs with the compound $3PbO{\cdot}Nb_2O_5$. When specimens of $3PbO{\cdot}Nb_2O_5$ are heated above the incongruent melting point, about 985° C, this tetragonal phase is observed to occur with the $5PbO{\cdot}2Nb_2O_5$ compound. Specimens of the 5 : 2 compound and compositions between 5 : 2 and 2 : 1 contain, upon quenching from above the solidus, red PbO solid solution plus a rhombohedral pyrochlore-type solid solution.

A specimen of the eutectic composition, 94 mole percent of PbO, showed almost entirely the red PbO solid solution when quenched from above the melting point. This specimen was put back in a sealed Pt tube and held overnight just below the melting point. The resulting product was an equilibrium mixture of yellow PbO and the compound $3PbO{\cdot}Nb_2O_5$. Thus the red PbO solid solution has been proven to be metastable.

There are several possible explanations of this nonequilibrium phenomenon. The most obvious conclusion would be that oxidation of PbO and reduction of Nb_2O_5 occur when they are heated together in a closed tube. However, this oxygen solid solution would then have parameters depending upon the amount of Nb_2O_5 present, which is not observed to be the case. Another possibility is that the tetragonal PbO solid solution represents the composition of the liquid in equilibrium at the temperature from which the material was quenched.

That is, the liquid when quenched devitrifies into a single-phase crystalline solid of the same composition. However, this explanation also would require different parameters of the solid solution for different temperatures and compositions. An alternative hypothesis is that the phase does not represent the equilibrium liquid but that the liquid follows its regular course of crystallization until it reaches the eutectic composition. This composition then crystallizes out as a single-phase nonequilibrium solid solution, having a structure similar to the low-temperature form of PbO.

It does not seem likely that this solid solution is of the substitutional type. The radius of Pb^{+2} is 1.20 A and that of Nb^{+5} is 0.69 A [23]. The ratio between the two is well beyond the limit at which even partial substitution might be expected. Therefore, it must be concluded that this nonequilibrium solid solution is of an interstitial type.

There is also the possibility that this apparent red PbO solid solution is a true compound in the system, having a minimum thermal stability at the temperature indicated here for the eutectic temperature, 835° C, and a composition equal to the hypothesized eutectic composition. That such a compound should have the same structure as red PbO seems highly unlikely and is not considered to be the true explanation of the observed phenomena.

6. Summary

The system PbO-Nb_2O_5 was studied by means of solid-state reactions, fusion characteristics, and X-ray diffraction data. The existence of six compounds in this system was shown. They are $3PbO{\cdot}Nb_2O_5$ which melts incongruently at about 985° C, $5PbO{\cdot}2Nb_2O_5$ which melts congruently at 1,220° C, $2PbO{\cdot}Nb_2O_5$ which melts congruently at about 1,233° C, $3PbO{\cdot}2Nb_2O_5$ which melts incongruently at about 1,233° C, $PbO{\cdot}Nb_2O_5$ which melts congruently at about 1,343° C, and $PbO{\cdot}2Nb_2O_5$ which melts congruently at about 1,337° C. The four eutectic points are located as follows: about 94 mole percent of PbO and 835° C, about 66 mole percent of PbO and 1,225° C, 41 mole percent of PbO and 1,310° C, and about 30 mole percent of PbO and 1,334° C.

Complete solid solution was noted between $2PbO{\cdot}Nb_2O_5$ and $5PbO{\cdot}2Nb_2O_5$. Partial solid solution occurred between the two compounds $PbO{\cdot}Nb_2O_5$ and $PbO{\cdot}2Nb_2O_5$. Nb_2O_5 accepts about 15 mole percent PbO in solid solution at the eutectic temperature. No solid solution occurs on either side of the compound $3PbO{\cdot}2Nb_2O_5$.

The rhombohedral-tetragonal inversion of $PbO{\cdot}Nb_2O_5$ was found to take place very sluggishly at approximately 1,150° C in a sealed Pt tube. The temperature of this phase transition is raised by the Nb_2O_5 solid solution to about 1,175° C.

A recent paper by M. H. Francombe and B. Lewis [24] suggests a solid-solution region from $PbO{:}1.5Nb_2O_5$ to $PbO{:}3Nb_2O_5$. This covers a range in which two phases have been found, for the most part, in the present work. No explanation can be found for the observation of such a large amount of solid solution in the PbO-Nb_2O_5 system.

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7. References

[1] G. Goodman, J. Am. Ceram. Soc. **36,** 368 (1953).
[2] M. H. Francombe, Acta Cryst. **9,** 683 (1956).
[3] W. R. Cook, Jr., and H. Jaffe, Phys. Rev. **88,** 1426 (1952).
[4] W. R. Cook, Jr., and H. Jaffe, Phys. Rev. **89,** 1297 (1953).
[5] B. Jaffe, R. S. Roth, and S. Marzullo, J. Research NBS **55,** 239 (1955) RP2626.
[6] R. F. Geller, P. J. Yavorsky, B. L. Steierman, and A. S. Creamer, J. Research NBS **36,** 277 (1946) RP1703.
[7] G. Brauer, Z. anorg. u. allgem. Chem. **248,** 1 (1941).
[8] F. Holzberg, A. Reisman, M. Berry, and M. Berkenblit, J. Am. Chem. Soc. **79,** 2039 (1957).
[9] A. Magneli and S. Lagergren, ASTM Index of X-ray Diffraction Data, Card No. 5–0379.
[10] F. Holzberg, Private communication.
[11] H. E. Swanson and R. K. Fuyat, NBS Circ. 539, Vol. II (1953).
[12] M. Petersen, J. Am. Chem. Soc. **63,** 2617 (1941).
[13] A. F. Efimov, V. A. Pchelkin, Yu. P. Simanov, E. P. Artamonova, and A. V. Lapitskii, Vestnik Moskov. Univ. **9,** No. 6, Ser. Fiz. Mat. i. Estestven Nauk No. 4, 77 (1954).
[14] R. S. Roth, Acta Cryst. **10,** 437 (1957).
[15] W. R. Cook, Bull. Am. Ceram. Soc. **37,** No. 4, Program, 33 (1958).
[16] W. R. Cook, Private communication.
[17] G. Shirane and R. Pepinsky, Phys. Rev. **92,** 504 (1953).
[18] J. K. Hulm, Phys. Rev. **92,** 504 (1953).
[19] F. Jona, G. Shirane, and R. Pepinsky, Phys. Rev. **98,** 903 (1955).
[20] R. F. Geller, A. S. Creamer, and E. N. Bunting, J. Research NBS **13,** 237 (1934) RP705.
[21] W. R. Cook, Private communication.
[22] R. S. Roth and L. W. Coughanour, J. Research NBS **55,** 209 (1955) RP2621.
[23] L. H. Ahrens, Geochim. Cosmochim. Acta **2,** 155 (1952).
[24] M. H. Francombe and B. Lewis, Acta Cryst. **11,** 696 (1958).

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Mass Spectra of Some Deuterostyrenes

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Mass spectra of alpha, beta, and para deuterostyrene; beta, beta dideuterostyrene; and alpha, beta, beta trideuterostyrene have been measured. The spectra are compared with the intensity distribution computed on the assumption of a random distribution of deuterium in C_8H_8. This gives a fair approximation to the observed spectra. The spectra of doubly charged styrenes are computed on the basis of observed half integer peaks in C_8H_8 and C_8H_7D. The metastable transition peaks of the deuterostyrenes have been recorded. It is suggested that ionized styrene molecules may form an octatetraene ring which dissociates with a random distribution of deuterium atoms but the observed spectra are not completely random and there may be other modes of fragmentation.

1. Introduction

The study of mass spectra of deuterium substituted hydrocarbons has been a rewarding field of research, for the distribution of deuterium atoms among the fragment ions gives information on the mechanism of ionization. The results have in many instances been unexpected and interesting. In simple paraffinic hydrocarbons the distribution of deuterium atoms in fragment ions seems to correspond to the structure of the molecule. This is the case in deuterium substituted butanes [1][1]. In other types of deuterated hydrocarbons there is more or less rearrangement of hydrogenic atoms in the ionization process and this is strikingly shown in aromatic hydrocarbons [2].

Five deuterium substituted molecules have been synthesized by Leo A. Wall [3] of the Polymer Structure Section. These were alpha, beta, and para deuterostyrene; beta, beta-dideuterostyrene; and alpha, beta, beta-trideuterostyrene. These styrenes were made over a period of years and the mass spectra were published in the American Petroleum Institute (API) catalog of mass spectral data [4]. It has seemed worthwhile to repeat the measurements under uniform conditions and present the results in a format convenient for intercomparison of results.

2. Experimental Procedure and Results

Measurements were made with a 180° Consolidated model 21–103 mass spectrometer under standard conditions of operation. Mass spectra reported in table 1 were recorded with a metastable suppressor set with an intermediate retarding field. Spectra were also recorded with the suppressor off to record the metastable transition peaks.

The deuterostyrenes were of good chemical purity and air was the only appreciable impurity. The isotopic purity was measured at low voltage to make the molecule ion predominant. The isotopic impurities ranged from 1 to 4 percent and were consistent with values given in the API catalog of mass spectra [4] except that the beta deuterostyrene was a much better sample than before. It contained about 4 percent of styrene.

Table 1 lists the singly charged ions of styrene and the five deuterostyrenes. The observed relative intensities have been corrected for the contribution of C^{13} isotopes, and for chemical and isotopic impurities. The 51, 52, and 53 peaks have been corrected for doubly charged ions on the basis of data in table 3. The corrections for chemical impurities may be subject to appreciable error. Peaks in the mass range 12 to 30 are small, and small inaccuracies in the air correction may explain some irregularities in relative intensities of peaks at masses 14 and 28.

Data of table 1 show that the mass spectra of the three monodeutero styrenes are similar and there is no close correlation between the position of deuterium in the molecule and the resulting spectrum. This suggests that there is a nearly random distribution of hydrogenic atoms in the fragment ions. Thus it is of interest to compare the observed spectra with spectra that would result from random removal of H and D atoms from C_8H_7D, $C_8H_6D_2$, and $C_8H_5D_3$.

Table 2 indicates how the computation is made for C_8H_7D. The numbers in parentheses denote the intensity of peaks in the C_8H_8 spectrum. Two different ions contribute to most of the peaks. The number of carbon atoms in the fragments does not enter into the computation, so the same relations hold for ions with 1 to 7 carbon atoms. In dideutero and trideutero styrene three different ions contribute to many of the peaks and the computations require more entries.

In table 1 columns 3, 7, and 9 headed "Computed C_8H_7D", etc., give these values computed from the C_8H_8 spectrum. It will be seen that in general the observed spectra are much like the spectra computed for a random distribution of D atoms in the fragment ions, although the agreement is far from exact.

2.1. Multiply Charged Ions

The API tables of styrene spectra [4] show half integer peaks in the mass range 25.5 to 53.5. These come from doubly charged ions of odd mass number. Table 3 lists the observed mass peaks at half integer mass numbers in the mass range 48.5 to 53.5. The other half integer peaks are very small and have been

[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *Mass spectra of styrene and deuterostyrenes* [a]

m/e	C_8H_8	Computed C_8H_7D	α-*d*-styrene	β-*d*-styrene	*p*-*d*-styrene	Computed $C_8H_6D_2$	ββ-d_2-styrene	Computed $C_8H_5D_3$	α-β,β-d_3 styrene
12	0.27	0.27	0.15	-------	0.22	0.27	-------	0.27	-------
13	.30	.26	.16	-------	.27	.22	0.11	.19	0.07
14	.26	.23	.36	-------	.23	.22	.06	.20	-------
15	.92	.64	.37	-------	.72	.45	.38	.29	.21
16	-------	.35	.24	-------	.14	.52	.47	.52	.23
17	-------	-------	-------	-------	-------	.21	.22	.50	.21
18	-------	-------	-------	-------	-------	-------	-------	.02	.14
24	.09	.09	.06	0.04	.09	.09	.07	.09	.08
25	.54	.47	.24	.15	.49	.41	.28	.34	.28
26	4.54	3.47	2.13	1.24	3.39	2.57	1.95	1.82	1.92
27	8.19	6.65	4.08	2.17	6.24	4.86	3.48	3.89	2.66
28	1.13	3.63	4.46	5.85	1.99	4.78	1.68	4.95	4.10
29	-------	0.56	0.09	0.07	0.45	1.52	2.86	2.67	1.56
30	-------	-------	-------	-------	-------	0.24	0.09	0.62	2.80
31	-------	-------	-------	-------	-------	-------	-------	.08	0.09
36	0.30	.30	.26	.23	.30	.30	.27	.30	.28
37	2.98	2.61	2.24	1.95	2.28	2.24	2.13	1.86	1.86
38	4.42	3.09	3.29	2.81	2.91	3.11	3.14	2.70	2.88
39	11.40	8.22	7.91	6.52	7.76	5.97	6.52	4.40	5.36
40	0.19	4.31	4.02	2.88	4.92	6.30	3.70	6.58	4.08
41	.27	0.20	0.18	0.18	0.84	1.36	2.02	3.13	2.77
42	-------	.17	.18	.14	.28	0.18	0.16	0.35	1.06
43	-------	-------	-------	-------	-------	.10	.36	.15	0.24
44	-------	-------	-------	-------	-------	.04	.06	.05	.12
48	.15	.15	.13	.14	.15	.15	.14	.15	.14
49	2.10	1.84	1.53	1.54	1.52	1.58	1.34	1.31	1.16
50	16.8	12.8	12.1	11.3	10.1	9.51	9.65	6.78	8.18
51	24.4	19.5	17.5	15.9	15.2	15.9	15.0	13.4	13.8
52	6.20	12.3	9.45	7.69	12.5	15.1	8.66	16.7	8.9
53	1.03	3.49	3.11	3.05	4.40	6.16	5.23	9.25	6.58
54	0.14	0.68	0.70	0.79	0.68	1.88	1.96	3.38	2.41
55	.01	.11	.10	.10	.23	0.43	0.64	1.00	1.60
56	-------	-------	-------	-------	-------	.07	.09	0.25	0.41
57	-------	-------	-------	-------	-------	-------	-------	.05	.15
60	.29	.29	.23	.25	.26	.26	.26	.29	.24
61	1.94	1.70	1.33	1.43	1.44	1.46	1.27	1.21	1.02
62	3.37	2.77	2.35	2.43	2.44	2.28	2.14	1.92	1.82
63	7.85	5.75	5.25	5.14	4.96	4.24	4.43	3.20	3.62
64	0.59	3.24	3.08	2.80	3.53	4.45	2.73	4.60	3.17
65	1.78	0.97	0.99	1.03	0.89	1.37	1.83	2.38	2.37
66	0.10	1.13	1.01	0.93	1.04	1.08	0.76	0.87	0.95
67	-------	0.08	0.04	.03	0.05	0.68	.69	1.00	.71
68	-------	-------	-------	-------	-------	.06	.02	0.37	.50
69	-------	-------	-------	-------	-------	-------	-------	.04	.02
72	.09	.09	.08	.09	.11	.09	.08	.09	.08
73	1.30	1.14	1.04	.96	1.21	.98	.80	.81	.76
74	6.47	5.01	4.37	4.32	3.78	3.68	3.39	2.80	2.79
75	4.02	4.13	3.53	3.50	4.02	4.21	3.41	4.18	3.11
76	4.38	3.70	3.24	3.27	3.31	3.32	2.75	3.15	2.35
77	20.8	9.98	9.89	9.57	7.40	5.15	5.83	3.33	3.84
78	38.2	22.5	22.1	23.1	19.8	13.4	14.1	7.51	6.84
79	0.43	28.7	21.6	20.7	29.4	23.8	21.6	15.5	18.7
80	-------	0.38	0.07	0.04	0.25	20.6	12.8	24.2	17.0
81	-------	-------	-------	-------	-------	0.32	0.06	13.8	8.68
82	-------	-------	-------	-------	-------	-------	-------	0.27	0.04
84	.09	.09	.08	.08	.10	.09	.08	.09	.09
85	.27	.24	.17	.18	.18	.20	.21	.17	.15
86	.42	.35	.29	.31	.27	.29	.33	.25	.27
87	.71	.54	.50	.48	.47	.43	.38	.34	.36
88	.06	.30	.26	.23	.33	.40	.28	.61	.31
89	2.25	.87	1.02	1.23	.48	.34	.92	.25	.35
90	0.02	1.41	1.08	0.86	1.64	1.21	.89	.63	.94
91	.37	0.07	0.05	.32	0.03	0.81	.72	1.20	.66
92	-------	.32	.03	.05	.42	.10	.03	0.41	.27
93	-------	-------	-------	-------	-------	.28	.01	.15	.18
94	-------	-------	-------	-------	-------	-------	-------	.23	.01
96	.02	.02	.03	.02	.03	.02	.04	.02	.02
97	.24	.21	.15	.16	.14	.18	.11	.15	.08
98	.89	.70	.54	.51	.50	.54	.33	.41	.22
99	.18	.33	.30	.35	.36	.44	.42	.51	.38
100	.05	.09	.08	.08	.08	.14	.13	.20	.15
101	.95	.38	.31	.27	.27	.15	.11	.09	.08
102	7.35	2.43	2.15	1.99	1.38	.78	.62	.27	.24
103	45.1	11.2	9.43	9.55	8.76	3.49	2.92	1.29	1.59
104	100	39.5	36.6	40.0	38.1	15.2	13.0	4.11	3.84
105	-------	100	100	100	100	33.9	36.6	19.6	16.7
106	-------	-------	-------	-------	-------	100	100	28.2	29.9
107	-------	-------	-------	-------	-------	-------	-------	100	100

[a] Under columns headed computed are given mass spectra of C_8H_7D, $C_8H_6D_2$, and $C_8H_5D_3$ computed from C_8H_8 assuming a random distribution of *d* atoms.

TABLE 2. *Computation of mass spectrum of* C_8H_7D *for random distribution of D in fragment ions of styrene* [a]

m/e	Ions	Intensity from C_8H_8 spectrum
105	C_8H_7D	(104)
104	C_8H_6D	$\frac{7}{8}$(103)
103	$C_8H_5D+C_8H_7$	$\frac{3}{4}$(102)+$\frac{1}{4}$(103)
102	$C_8H_4D+C_8H_6$	$\frac{5}{8}$(101)+$\frac{1}{4}$(102)
101	$C_8H_3D+C_8H_5$	$\frac{1}{2}$(100)+$\frac{3}{8}$(101)
100	$C_8H_2D+C_8H_4$	$\frac{3}{8}$(99) +$\frac{1}{4}$(100)
99	$C_8HD+C_8H_3$	$\frac{1}{4}$(98) +$\frac{5}{8}$(99)
98	$C_8D+C_8H_2$	$\frac{1}{8}$(97) +$\frac{3}{4}$(98)
97	C_8H	$\frac{7}{8}$(97)

[a] Numbers in parentheses denote intensity of designated ion in C_8H_8 spectrum

omitted. In this mass range the ions of even molecular weight which give integral half mass numbers are masked by singly charged ion peaks. The half integer peaks of the three monodeuterostyrenes are much alike and table 3 gives the mean values of these.

Since C_8H_8 has an even molecular weight while C_8H_7D has an odd molecular weight the half integer peaks of the two spectra in a sense complement each other. On the assumption that there is a random distribution of D in the fragment ions, the integral mass peaks in the two spectra can be computed from the observed half integer peaks using the relations of table 2. These computed values are given in parentheses in table 3. From the complete spectrum of $C_8H_8^{++}$ the complete spectra of $C_8H_6D_2^{++}$ and $C_8H_5D_3^{++}$ can be computed. The computed half integer peaks are in general in very good agreement with the observed peaks and this justifies the assumptions made in computing the $C_8H_8^{++}$ spectrum. The intensity distribution in this spectrum is quite unusual. Commonly in aromatic compounds the doubly-charged molecule ion is the most abundant of the doubly charged ions.

TABLE 3. *Doubly charged ions of styrenes* [a]

m/e	C_8H_8	C_8H_7D (mean)	$C_8H_6D_2$	$C_8H_5D_3$
48.5	0.04	0.02	0.02	0.01
49	(0.44)	(0.33)	(0.25)	(0.17)
49.5	0.30	0.30	0.29(0.30)	0.24(0.28)
50	(0.64)	(0.43)	(0.32)	(0.26)
50.5	0.13	0.37	0.37(0.41)	0.30(0.35)
51	(7.55)	(1.97)	(0.48)	(0.32)
51.5	0.27	5.71	4.12(3.3)	1.04(0.93)
52	(2.88)	(0.24)	(4.12)	(4.05)
52.5	------	2.88	0.21(0.20)	2.87(2.81)
53	------	--------	(2.88)	(0.17)
53.5	------	--------	----------	3.00

[a] Values in parentheses have been computed on the assumption that there is a random distribution of H and D in the fragment ions.

In the C_8H_8 spectrum a sharply defined peak at 34.7 mass units of relative intensity 0.01 percent is a triply charged molecule ion. The corresponding peaks at 35.0, 35.3, and 35.7 are found in the spectra of C_8H_7D, $C_8H_6D_2$, and $C_8H_5D_3$. These ions have not been reported before.

2.2 Metastable Transition Peaks

Mass spectra of the deuterostyrenes were recorded with the metastable suppressor voltage off to detect metastable transition peaks. In the C_8H_8 spectrum there is a conspicuous broad peak at apparent mass 58.5 which comes from the delayed transition

$$104^+ \longrightarrow 78^+ + 26$$

of relative intensity 0.07 percent. This peak has a broad flat maximum and the "half width" (width between points of ordinate half the maximum value) is 2.1 mass units. The corresponding peaks in the three C_8H_7D molecules have a "half width" of about 2.5 mass units and the midpoint is about 59.1. This is the unresolved effect of two transitions with $C_8H_7D^+$ losing C_2H_2 or C_2HD to give $C_6H_5D^+$ and $C_6H_6^+$. The apparent masses are 59.4 and 58.0.

The dideuterostyrene has a peak of "half width" 3.5 mass units with the midpoint near 59.6. This is the superposed effect of three peaks at 60.4, 58.8, and 57.4 mass units. The trideuterostyrene has a peak of "half width" 3.2 mass units with the midpoint near 60.1. It is the unresolved effect of three peaks of apparent masses 61.3, 59.8, and 58.3.

Another metastable transition, conspicuous in these spectra, comes from the loss of one H atom from the molecule ion. In the C_8H_8 spectrum this gives a broadened 102 peak from $104^+ \longrightarrow 103^+ + 1$. This is seen best when the metastable suppressor is used, for the retarding field is not sufficient to stop an ion differing by only one percent from the kinetic energy of the 102^+ ion. With the suppressor on there is a distinct shoulder on the high mass side of the 102 peak near the top of the broader metastable peak. The relative intensity is 0.7 percent. The deuterostyrenes show the same breaks on the corresponding peaks 103, 104, and 105.

In the C_8H_8 spectrum reported in the API catalog serial no. 359 [4] the 58.5 peak has nearly 10 times the relative intensity observed here. Another transition of much lower intensity at 33.8 which was not seen in this work was ascribed to the transition

$$77^+ \longrightarrow 51^+ + 26.$$

The differences in measured intensity are ascribed to characteristics of the type 102 and type 103 mass analysers used in the early work and in this research.

3. Discussion

The data of table 1 indicate that there is a roughly random distribution of deuterium atoms in the mass spectra of the deuterostyrenes. The agreement is far from exact but the results are in marked contrast to the pattern that would result from simple fragmentation of styrene. Thus $C_6H_6^+$ is one of the more abundant ions and this suggests that the phenyl ring remains intact and that the alpha hydrogen moves to the ring when C_2H_2 is removed from the

molecule. If this were true β-*d*-styrene would give $C_6H_6^+$ while *p*-*d*-styrene and α-*d*-styrene would give $C_6H_5D^+$. This is not the case, for the 79 peak is large in all three spectra, although both α and β deuterostyrene give a 79 peak somewhat smaller than the computed abundance for random distribution.

In the metastable transitions giving $C_6H_6^+$ and $C_6H_5D^+$ from $C_8H_7D^+$ the two peaks are not resolved but the three monodeuterostyrenes give a similar distribution of intensity in the broad peaks showing a similar distribution of deuterium atoms in the fragment ions. If β-deuterostyrene and β, β-dideuterostyrene dissociated by losing C_2HD and C_2D_2, respectively, then the apparent masses would be 58.0 and 57.4 as compared with 58.5 for $C_8H_8^+$. The observed values are 59.1 and 59.6.

The fragmentation of alkylaromatics has been studied rather carefully by Meyerson and Rylander [2,5,6] using spectra of isotopically labeled molecules and considerations of energetics of ion formation in their study. They suggest that formation of a tropylium ion (cyclic $C_7H_7^+$) is an intermediate step in the fragmentation.

This suggests that formation of a cyclooctatetraene ion may be an intermediate step in the fragmentation of styrene. The spectrum of cyclooctatetraene has been published in the API catalog [7]. The intensity of all the fragment ions is roughly twice that observed in styrene but there is a close parallelism in the relative intensities. Metastable transition peaks at 102, 58.5, and 33.8 are the same delayed transitions that are found in styrene. A fourth peak is reported at 34.7 but this is probably the triply charged ion, not a metastable transition. It is interesting that in both mass spectra $C_8H_6^+$ is one of the most abundant fragment ions (82% in the cyclic and 38% in styrene). In the case of cyclooctatetraene the fragment ion $C_6H_6^+$ is probably not a benzene ion and it follows that $C_6H_6^+$ of styrene is not necessarily a benzene ring.

If styrene ions form an octatetraene ring and then dissociate, the distribution of D should be completely random. This is not the case, although the random distribution gives a good approximation to the observed distribution. There may be alternative modes of dissociation into fragment ions. This would not be surprising but it suggests that it would be of some interest to study the distribution of D atoms at low voltage near the threshold for appearance of fragment ions.

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4. References

[1] Am. Petrol. Inst., Catalog of mass spectral data serial numbers 430, 431, 837, and 838.
[2] P. N. Rylander, S. Meyerson, and H. M. Grubb, J. Am. Chem. Soc. **79,** 842 (1957).
[3] L. A. Wall and D. W. Brown, J. Phys. Chem. **61,** 129 (1957).
[4] Am. Petrol. Inst., Catalog of mass spectral data serial numbers 359 and 1289 to 1293.
[5] S. Meyerson and P. N. Rylander, J. Chem. Phys. **27,** 901 (1957).
[6] P. N. Rylander and S. Meyerson, J. Chem. Phys. **27,** 1116 (1957).
[7] Am. Petrol. Inst., Catalog of mass spectral data serial number 690.

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Heat of Reaction of Diborane with Water and the Heat of Formation of Boric Oxide

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The heat of reaction of gaseous diborane with water to form gaseous hydrogen and a solution of boric acid ($H_3BO_3+1{,}000H_2O$) has been measured by passing gaseous diborane through two successive bubblers in a calorimeter. The heat of the reaction obtained was:

$$\Delta H_{298.15} = -466.34 \pm 2.26 \text{ kj/mole } (-111.46 \pm 0.54 \text{ kcal/mole}).$$

Combination of this value with values previously reported for the heat of decomposition of diborane and the heat of solution of boric oxide yields the following value for the heat of formation of crystalline boric oxide from amorphous boron and gaseous oxygen:

$$\Delta Hf_{298.15} = -1280.89 \pm 3.14 \text{ kj/mole } (-306.14 \pm 0.75 \text{ kcal/mole}).$$

1. Introduction

The determination of the heat of formation of boric oxide glass by the combustion of boron in oxygen has led to values which range from −279.9 to −368 kcal/mole. Roth and Börger [1,2][1] obtained a value of −340 ±3 kcal/mole from the combustion of boron in an oxygen bomb with paraffin oil as an auxiliary substance to aid the reaction. Robertson [3] obtained a value of −368 ±17 kcal/mole from the combustion of boron in an oxygen bomb using no auxiliary substance other than a cotton string fuse. Todd and Miller [4] obtained a value of −338.4 ±0.8 kcal/mole from the combustion of boron in an oxygen bomb with benzoic acid as an auxiliary substance. Eggersgluess, Monroe, and Parker [5] obtained a value of −281.1 ±3.1 kcal/mole from the combustion of boron in an oxygen bomb with paraffin oil and lamp black as auxiliary substances. In all of these determinations, complete combustion of the boron was not achieved and the amount of reaction was determined from a titration of the boric acid formed by dissolving the soluble products of combustion in water. Nathan [6] obtained a value of −306 ±3 kcal/mole from the combustion in an oxygen bomb using iron wire as an auxiliary substance. In this case complete combustion of the boron was achieved although the over-all uncertainty was rather high. Bichowsky and Rossini [7] calculated a value of −279.9 kcal/mole for the heat of formation of boric oxide glass from the data existing in the literature prior to 1934.

An investigation of the combustion of powdered amorphous boron (obtained from experiments on the decomposition of diborane) in an oxygen bomb has been made. It was found possible to ignite the boron with a fuse of iron wire, but complete combustion of the boron was not obtained. The addition of relatively large quantities of benzoic acid did not effect the complete combustion of the boron. It has been shown that neither the titration of the solution formed by dissolving in water the boric oxide formed in the combustion, nor the difference in weight of the boron placed in the bomb and the residue remaining after combustion, gives a true measure of the amount of reaction. Large amounts of boron oxide remain in the residue even after washing with warm water or digesting with hydrochloric acid. This has been verified by passing chlorine over the residue in a hot quartz tube, according to the method of Winslow and Liebhafsky [8]. In such an experiment with pure boron, all the boron was carried away as boron trichloride. After similar treatment of the residues from the bomb combustion there remained large amounts of a white or gray material.

A method free from many of the difficulties encountered in the combustion of boron is the measurement of the heat of hydrolysis of diborane according to reaction (1), since the heat of formation of diborane and the heat of solution of boric oxide are known.

$$B_2H_{6(gas)}+6H_2O_{(liq)}+aq=2H_3BO_{3(aq)}+6H_{2(gas)}. \quad (1)$$

Roth, Börger, and Bertram [9] measured the heat of hydrolysis by breaking ampoules filled with gaseous diborane under water in a bomb. They obtained a value of −108 kcal/mole for the reaction going to $[H_3BO_3+1{,}000H_2O]$. However, owing to the uncertainties in the analyses and in obtaining complete reaction under these conditions, their value is probably in error by several kilocalories.

2. Materials

The diborane used in this investigation was supplied by the Naval Research Laboratory through the courtesy of R. R. Miller. A sample supplied to the Ohio State University was found by the cryoscopic method to have a purity of 99.95 mole percent [10].

[1] Figures in brackets indicate the literature references at the end of this paper.

3. Apparatus

3.1. Calorimetric System

A submarine-type calorimeter, built by the Precision Scientific Company, was used for these experiments. It consists of a nickel-plated copper calorimeter "can" having a volume of 5 liters, fitted with a stirrer and lid and supported within a Monel calorimeter "well" by three plastic pegs so that there is a ½-in. air space between the can and well at all points. The well is fitted with a rubber gasket and a nickel-plated brass cover held in place by six clamp-screws. The thermometer, calorimeter stirrer, heater leads, and connections to the calorimetric reaction vessel pass through tubes attached to the well cover; these tubes prevent water from entering the well when the assembly is lowered into the water bath.

The container for the water bath is made of Monel and has double walls separated by 1 in. of cork insulation; it has a volume of 46.5 liters. Two synchronous motors are provided; one operating at 1,700 rpm is used for circulating the water in the bath, the other, operating at 300 rpm, is used for stirring the water in the calorimeter. Ice water circulated through a coil in the bath provides a slight excess of refrigeration; a 100-w heating coil is provided for temperature control. The general characteristics of this type of calorimeter have been described in detail by Dickinson [11].

A servomechanism arranged as an on-off controller was used to maintain the water bath at a constant temperature. The sensing element consisted of a 28-ohm platinum resistance thermometer which formed one arm of a Wheatstone bridge circuit; the other arms consisted of two 500-ohm and one 29-ohm coils of manganin. A variable resistor placed in parallel with the 29-ohm coil was used to select the desired temperature to be maintained.

The glass reaction vessel used in these experiments is shown in figure 1. It consisted of a two-stage bubbler and a helical coil in which the exit gases were cooled to the calorimeter temperature. The large bubbler contained 275 ml of water and the small bubbler contained 100 ml of water. Each bubbler was fitted with a porous corundum frit to produce very small bubbles. The connection between the bubblers was fitted with a vent by which the pressures within the vessels could be equalized at the end of the experiment.

The calorimeter heater consisted of a manganin coil, having a resistance of 121 ohms, wound non-inductively between two thin-walled concentric copper cylinders and insulated from the cylinders by means of mica sheets. The cylinders were approximately 1½ in. in diameter and 5 in. in length. The inner cylinder was offset at the ends to form a close fit with the outer cylinder; after introducing the heating coil, the ends were sealed by soldering the cylinders together. The heater was nickel plated to avoid corrosion by the water. The heater leads passed through a copper tube soldered to the outer cylinder; the heater was suspended from the calorimeter lid by means of a flange soldered to the end of this tube.

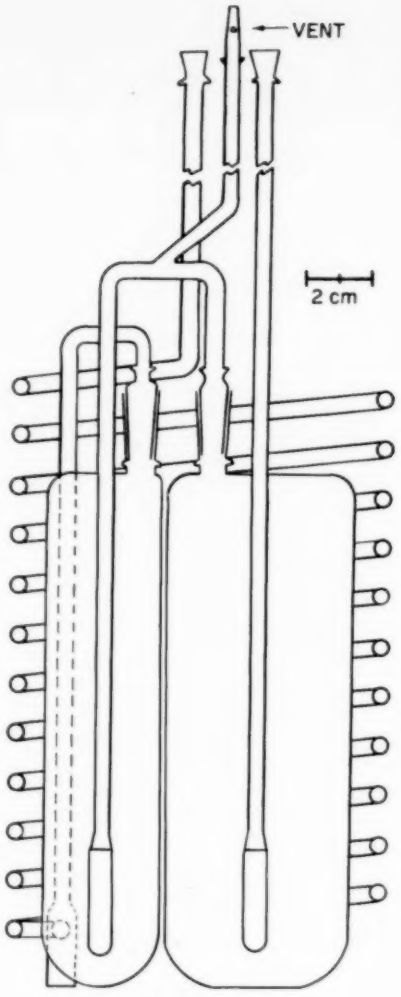

FIGURE 1. *Reaction vessel.*

3.2. Thermometric System

A calorimetric-type platinum resistance thermometer was used for these experiments, the resistance of this thermometer was 25.546 ohms at 0° C. Thermometer resistances were measured using a G–2 Mueller bridge in conjunction with a high-sensitivity galvanometer. Readings on the galvanometer scale were made to the nearest 0.5 mm which corresponded to 50 microdegrees C.

3.3. Apparatus for Measurement of Electrical Energy

The electrical energy used for the calibration experiments was obtained from a 120-v storage battery from which no other current was drawn

during the progress of these experiments. The quantity of electrical energy was determined from measurements of the current through the calorimeter heater, the potential drop across the heater, and the time during which the current flowed. The potential drop across the heater was determined from the potential drop across a 10-ohm standard resistor, which was connected in series with a 10,000-ohm standard resistor, both in parallel with the calorimeter heater. The total current was determined from the potential drop across a 0.1-ohm standard resistor, placed in series with the calorimeter heater. Correction for the quantity of current flowing through the parallel circuit gave the actual current flowing through the calorimeter heater. The potential measurements were determined using a Wenner potentiometer, balanced against a thermostated Weston standard cell. The potentiometer ratio was determined [12] at the time of each experiment in a manner previously described [13]. The resistance thermometer, bridge, potentiometer, standard resistors, and the standard cell were all calibrated in terms of standards maintained at the Bureau.

An automatic solenoid switch [14], actuated by an impulse from the standard seconds signals produced at the Bureau, served to switch the current from an external resistor into the calorimeter heater at the start of the heating period and to interrupt the current at the close of the heating period. The over-all error in timing by this procedure did not exceed 0.01 sec.

The electrical energy was computed as the product of the current through the heater, the potential drop across the heater and the time during which the current passed through the heater.

4. Procedure

The bubblers were filled with 275 and 100 g of water, and the hydrolysis vessel was assembled. The calorimeter can containing 4,687.63 g of water was placed in the calorimeter well after which the hydrolysis vessel and calorimeter heater were introduced and the can cover attached. The well cover was then secured, the assembly was lowered into the water bath, the calorimeter stirrer connected, and the platinum thermometer inserted. The inlet and exit tubes of the vessel were then connected to the gas train and air was removed by flushing with helium.

The cylinder containing the diborane was cooled in liquid nitrogen and the diborane degassed to remove any hydrogen which may have been present as a decomposition product. The liquid nitrogen was then replaced by "dry ice" to maintain the diborane at approximately $-80°$ C; at this temperature the vapor pressure of diborane is approximately 2 atm.

The jacket (or water bath) was warmed to 27.00° C and the jacket control adjusted to maintain this temperature within $\pm 0.001°$ C. The temperature of the water in the calorimeter was adjusted to 26.00° C by means of the calorimeter heater.

The calorimetric temperature observations were made at 2-min intervals during a 20-min "fore" rating period, at 1-min observations during a 60-min "reaction" period, and at 2-min intervals during a 20-min "after" rating period. Diborane was passed slowly into the hydrolysis vessel at the start of the reaction period. After about 30 min the diborane cylinder was closed and the vessel was flushed with helium for about 30 min.

The water vaporized from the hydrolysis vessel during the reaction period by the helium and hydrogen gases was collected in a weighed absorption tube containing magnesium perchlorate and phosphorus pentoxide. A correction was applied to the observed temperature rise for the heat of vaporization of this quantity of water. The hydrogen that was evolved in the hydrolysis passed through the first absorption tube, was burned to water in a copper-oxide furnace heated to 600° C, and was collected in a second absorption tube. The quantity of reaction was determined from this mass of water. The temperatures of the diborane and helium gases which entered the system during the reaction period were observed at 1-min intervals. The total quantity of helium was calculated from the mass of water in the first absorption tube on the assumption that the exit gases were saturated with water vapor at the mean temperature of the calorimeter. Only an approximate value for the quantity of helium was necessary in order to evaluate the correction for the gas heat capacity.

The electrical calibration experiments were carried out in the same manner except the diborane was omitted and a carefully measured quantity of electrical energy was introduced through the calorimeter heater. Measurements of the current through the heater and the potential drop across the heater were made on alternate minutes during the heating period. In a few of the calibration experiments the helium was omitted in order to test for systematic errors in the vaporization correction and to show whether or not the stirring caused by the bubbling of the helium through the water was necessary to obtain thermal equilibrium at the end of the experiment. Although no systematic errors were discovered it was found that a considerably longer period of time was required to obtain thermal equilibrium when the helium was omitted.

At the end of each reaction experiment the pressures in the bubblers were equalized by opening the vent to prevent transfer of solution. The concentrations of boric acid in the bubblers were determined by titration with standard alkali in the presence of mannitol. Traces of crystalline boric acid, usually found in the connection between the bubblers, were washed out and the quantity determined in a separate titration. Agreement within the limits of the accuracy of titration was obtained between the stoichiometric amounts of boric acid and hydrogen. However, the amount of hydrogen oxidized to water was used as the measure of the quantity of reaction because this determination was more precise than the boric acid titration.

5. Results and Calculations

The quantity of reaction was determined from the mass of hydrogen (as water) produced. This quantity of reaction was associated with a release of q joules of energy given by the relationship

$$(\Delta Rc)(E_s)=q,$$

where ΔRc is the corrected temperature rise in ohms [15] and E_s is the energy equivalent of the calorimetric system expressed in joules per ohm. The value q, when corrected for the heat of vaporization of water $q_{(vap)}$, the heat of dilution of the solutions to an arbitrary standard concentration $q_{(dil)}$, the heat of solution of the crystalline boric acid $q_{(soln)}$, and the heat capacities of the gases involved q_g yields q_c, the corrected quantity of heat for m moles of reaction under standard conditions. The heat of reaction is the ratio of q_c to m or

$$\Delta H=q_c/m \text{ joules/mole.}$$

To convert to the conventional thermochemical calorie, the following relationship was used: 1 cal =4.1840 j.

Two sets of data were taken using two slightly different calorimetric systems and two separate samples of diborane. The results of the electrical energy calibration experiments are given in table 1. The results for the diborane reaction experiments are given in table 2. The final value for the heat of reaction was obtained as the mean of the experimental values and the uncertainty assigned was taken as twice the standard deviation of the experimental values combined with reasonable estimates of all known sources of error.

The value for the correction for the heat of dilution of boric acid was taken from the data of Davis, Mason, and Stegeman [16]. The value used for the correction for the heat of solution of boric acid was taken as 5.18 kcal/mole [9,17,18,19,20]. The value used for the heat of vaporization of water was 10.514 kcal/mole [21].

TABLE 1. *Results of the electrical calibration experiments*

Experiment No. and system	E	$q_{(vap)}$	q_g	E_s	ΔRc	E_s
	j	*j*	*j*	*j*	*Ohm*	*j/ohm*
1A	41927.4			41927.4	0.192731	217544
2A	43375.1			43375.1	.199382	217548
3A	43552.1			43552.1	.200303	217431
4A	41384.9	−50.6	−1.5	41332.8	.190016	217523
5A	42583.2	−32.6	−0.9	42549.7	.195647	217482
Mean						217506
Standard deviation of the mean						±22
1B	9425.9	−142.8	+1.0	9284.1	0.042273	219622
2B	7994.8	−123.7	1.5	7872.6	.035877	219433
3B	8743.5	−126.4	−2.6	8614.5	.039173	219909
4B	7802.4	−129.4	−0.8	7762.2	.035266	220104
5B	7558.9	−311.9	−5.7	7241.3	.032934	219540
Mean						219722
Standard deviation of the mean						±124

TABLE 2. *Results of the diborane reaction experiments*

Experiment No. and system	ΔRc	q	$q_{(vap)}$	$q_{(dil)}$	$q_{(soln)}$	q_g	B_2H_6	$-\Delta H$ (25° C)
	Ohm	*j*	*j*	*j*	*j*	*j*	*Moles*	*kj/mole*
1A	0.029524	6421.6	195.7	−0.3	−6.1	−4.5	0.014154	466.75
2A	.007319	1591.9	84.0	+0.1	−4.8	−2.5	.003561	468.60
3A	.034260	7451.8	208.5	−0.4	−24.0	−6.7	.016295	468.19
4B	.034767	7639.1	193.3	−0.9	−18.3	−1.4	.016890	462.51
5B	.042940	9434.9	191.9	−1.5	−18.5	−3.2	.020625	465.63
Mean								466.34
Standard deviation of the mean								±1.10

The data yield the following value for the heat of reaction of diborane with water:

$$B_2H_{6(g,\ 1\ atm)}+6H_2O_{(liq)}+[2{,}000H_2O]_{(liq)}=2\ [H_3BO_3+1{,}000H_2O]_{(soln)}+6H_{2(g,\ 1\ atm)} \quad (2)$$

$$\Delta H_{298.15}=-466.34\ \pm 2.26 \text{ kj/mole}$$
$$=-111.46\ \pm 0.54 \text{ kcal/mole.}$$

The reference state of 1 mole of boric acid in 1,000 moles of water was selected instead of infinite dilution because of lack of data on heats of dilution in the very dilute range where ionization energies may become important.

The heat of formation of boric oxide can be calculated by combining the heat of reaction for eq (2) with the heat of formation of diborane

$$2B_{(amorph)}+3H_{2(g)}=B_2H_{6(g)} \quad (3)$$
$$\Delta Hf_{298.15}=6.73\pm 0.52 \text{ kcal/mole} \quad [22],$$

and with the following values taken from the available literature:

$$H_{2(g)}+1/2\ O_{2(g)}=H_2O_{(liq)} \quad (4)$$
$$\Delta Hf^\circ_{298.15}=-68.317\ \pm 0.007 \text{ kcal/mole} \quad [21],$$

$$B_2O_{3(amorph)}+3H_2O_{(liq)}+[2{,}000H_2O]_{(liq)}=2[H_3BO_3+1{,}000H_2O]_{(soln)} \quad (5)$$
$$\Delta H_{298.15}=-7.90\ \pm 0.03 \text{ kcal/mole} \quad [9,17,18,19],$$

$$B_2O_{3(c)}=B_2O_{3(amorph)} \quad (6)$$
$$\Delta H_{298.15}=4.36\ \pm 0.02 \text{ kcal/mole} \quad [23],$$

$$B_{(c)}=B_{(amorph)} \quad (7)$$
$$\Delta H_{298.15}=0.4\ \pm 0.1 \text{ kcal/mole} \quad [21].$$

The following heats of formation of boric oxide are obtained from these values:

$$2B_{(amorph)}+3/2\ O_{2(g)}=B_2O_{3(amorph)} \quad (8)$$
$$\Delta Hf_{298.15}=-1262.65\ \pm 3.14 \text{ kj/mole}$$
$$=-301.78\ \pm 0.75 \text{ kcal/mole,}$$

$$2B_{(amorph)}+3/2\ O_{2(g)}=B_2O_{3(c)}$$
$$\Delta Hf_{298.15}=-1280.89\ \pm 3.10 \text{ kj/mole}$$
$$=-306.14\ \pm 0.74 \text{ kcal/mole,}$$

$$2B_{(c)}+3/2\ O_{2(g)}=B_2O_{3(amorph)}$$
$$\Delta Hf_{298.15}=-1259.30\ \pm3.14\ \text{kj/mole}$$
$$=\ -300.98\ \pm0.75\ \text{kcal/mole},$$

$$2B_{(c)}+3/2\ O_{2(g)}=B_2O_{3(c)}$$
$$\Delta Hf°_{298.15}=-1277.54\ \pm3.14\ \text{kj/mole}$$
$$=\ -305.34\ \pm0.75\ \text{kcal/mole}.$$

6. Discussion

This determination of the heat of formation of boric oxide has several distinct advantages over the regular bomb combustion procedure. With this procedure there is no uncertainty regarding the nature and state of the reaction products. When boron is burned in an oxygen bomb it is necessary to employ some auxiliary substance in order to obtain a reasonable quantity of reaction. In order for this auxiliary material to be effective it must prevent the molten boric oxide from covering the remainder of the boron which would terminate the reaction and leave an insoluble residue. When the auxiliary substance contains hydrogen the water formed in the combustion will react with the boric oxide to form boric acid. It then becomes necessary to estimate the amounts of boric oxide and boric acid present in the bomb after the combustion as well as the degree of solution of boric acid. These cannot be accurately determined from the theoretical quantity of water produced since a considerable portion condenses on the walls and head of the bomb. When a material containing no hydrogen is employed there is the further possibility that some of the boron alloys with the substance used; this portion then fails to burn.

The accuracy of the method described in this paper is limited only by the combined uncertainties in the measurements, since there can be little doubt as to the nature and state of the reaction products.

7. References

[1] W. A. Roth and E. Börger, Ber. [B] **70,** 48 (1937).
[2] W. A. Roth, Z. Naturforsch **1,** 574 (1946).
[3] J. A. Robertson, Thesis, Cornell University (1944).
[4] B. J. Todd and R. R. Miller, J. Am. Chem. Soc. **68,** 530 (1946).
[5] W. Eggersgluess, A. G. Monroe, and W. G. Parker, Trans. Faraday Soc. **45,** 661 (1949).
[6] C. C. Nathan, Thesis (University of Pittsburgh, 1948).
[7] F. R. Bichowsky and F. D. Rossini, The thermochemistry of the chemical substances (Reinhold Publishing Corp., New York, N. Y., 1936).
[8] E. H. Winslow and H. A. Liebhafsky, J. Am. Chem. Soc. **64,** 2725 (1942).
[9] W. A. Roth, E. Börger, and A. Bertram, Ber. [B] **70,** 971 (1937).
[10] E. M. Carr, J. T. Clarke, and H. L. Johnston, J. Am. Chem. Soc. **71,** 740 (1929).
[11] H. C. Dickinson, Bul. BS **11,** 189 (1914) S230.
[12] N. S. Osborne, H. F. Stimson, and D. C. Ginnings, J. Research NBS **23,** 197 (1939) RP1228.
[13] E. J. Prosen, F. W. Maron, and F. D. Rossini, J. Research NBS **46,** 106 (1951) RP2181.
[14] E. J. Prosen and F. D. Rossini, J. Research NBS **33,** 255 (1944) RP1607.
[15] F. D. Rossini, Experimental thermochemistry, p. 136 (Interscience Publishers, Inc., New York, N. Y., 1956).
[16] W. D. Davis, L. S. Mason, and G. Stegeman, J. Am. Chem. Soc. **71,** 2775 (1949).
[17] E. R. Van Artsdalen and K. P. Anderson, J. Am. Chem. Soc. **73,** 579 (1951).
[18] J. Smisko and L. S. Mason, J. Am. Chem. Soc. **72,** 3629 (1950).
[19] M. von Stackelberg, F. Quatrum, and J. Dressel, Z. Elektrochem. **43,** 14 (1937).
[20] C. Katz, Thesis (Cornell University, 1949).
[21] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, Selected values of chemical thermodynamic properties, NBS Circ. **500,** (U. S. Government Printing Office, Washington 25, D. C., 1952).
[22] E. J. Prosen, W. H. Johnson, and F. Y. Pergiel, J. Research NBS, **61,** 247 (1958) RP2901.
[23] J. C. Southard, J. Am. Chem. Soc. **63,** 3174 (1941).

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Heat of Formation of Titanium Tetrachloride

Walter H. Johnson, Raymond A. Nelson, and Edward J. Prosen

The heat of formation of gaseous titanium tetrachloride has been measured by the reaction of metallic titanium with gaseous chlorine in a calorimeter. The value for the heat of formation obtained in this investigation corresponds to the reaction:

$$Ti_{(c)} + 2Cl_{2(g)} = TiCl_{4(g)},$$

$$\Delta Hf\ °(25°\ C) = -763.2 \pm 2.9\ kj/mole\ (-182.4 \pm 0.7\ kcal/mole).$$

Earlier data are discussed briefly.

1. Introduction

This investigation is part of a program on the determination of the thermodynamic properties of titanium compounds sponsored by the Office of Naval Research; it is also a part of the work of the thermochemical laboratory of the Bureau on the determination of the heats of formation of compounds of importance to science and industry.

The heat of formation of $TiCl_4$ may be obtained by several different methods, each having certain advantages and disadvantages. Titanium tetrachloride hydrolyzes rapidly in water forming aqueous hydrochloric acid and titanium dioxide; under these conditions, however, it is difficult to determine the thermodynamic state of the precipitated TiO_2. Metallic titanium will react at room temperature with liquid chlorine, or with chlorine gas under pressure to form the tetrachloride. In either case, the observed heat of reaction is complicated by the mutual heats of solution and vaporization of the tetrachloride and chlorine.

Metallic titanium reacts rapidly with an excess of chlorine under atmospheric pressure at about 300° C to produce gaseous $TiCl_4$. In this case there is no uncertainty regarding the thermodynamic state of the reactants and products and the process is well defined. It is necessary, however, to measure accurately the fairly large amount of energy required to maintain the reaction temperature. Since the uncertainty in this measurement can be evaluated quite accurately, the direct reaction between metallic titanium and gaseous chlorine was selected for measurement.

2. Source and Purity of Materials

The titanium sample was obtained by reduction of the iodide and was supplied by the Naval Research Laboratory (courtesy of E. J. Chapin). This sample was taken from material for which the purity was stated to be in excess of 99.99 percent.

The chlorine was obtained from the Matheson Company. The gas phase existing at the boiling point of liquid nitrogen was analyzed by means of the mass spectrometer by Shuford Schuhmann of the Gas Chemistry Section of the Chemistry Division. The following results were obtained in volume percent: H_2, 0.00; CO, 0.00; (N_2+O_2+A), 0.01. The purity of a second sample was determined to be 99.99 mole percent from cryoscopic measurements by Gaylon S. Ross of the Pure Substances Section of the Chemistry Division.

A sample of the helium, taken directly from the cylinder, was found to contain less than 0.01 percent of oxygen and nitrogen from an analysis by Vernon H. Dibeler of the Mass Spectrometry Section of the Atomic and Radiation Physics Division.

3. Apparatus

The glass reaction vessel (fig. 1) consisted of a quartz tube, closed at the bottom, upon which was wound a 139-ohm manganin heating coil, surrounded by a vacuum jacket. The jacket was silvered on the inside to reduce the amount of energy transferred by radiation. The sample was placed in a quartz crucible on the bottom of the quartz tube. Chlorine was admitted through a centrally located quartz inlet tube that extended down into the crucible so that the gas was directed against the hot sample. The exit gases passed out through a glass helix in which they were cooled to the temperature of the calorimeter.

The calorimeter was of the isothermal jacket type similar to that described previously [1][1] except that a smaller calorimeter can and well were used, which resulted in a considerably lower energy equivalent. The temperature of the calorimeter jacket was maintained constant at 27° C within ±0.001° C. The thermometric system and the apparatus for measurement of electrical energy have been described in a previous report [2]; all equipment was calibrated in terms of standards maintained at the Bureau.

The gas train used in these experiments is shown in figure 2. The helium was passed successively through heaters containing sponge titanium and copper oxide at 600° C and through absorbers containing Ascarite, magnesium perchlorate, and phosphorus pentoxide. The chlorine was dried by passing it through an absorber containing phosphorus pentoxide. Valves were provided whereby either

[1] Figures in brackets indicate the literature references at the end of this paper.

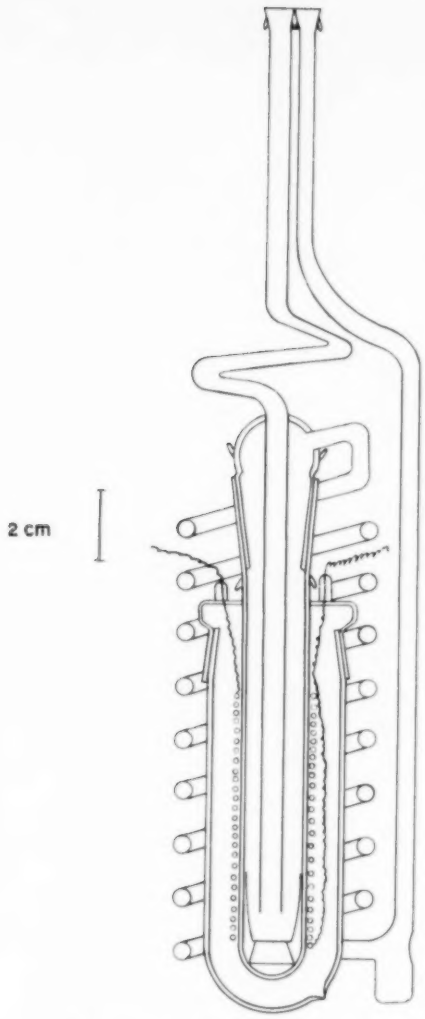

FIGURE 1. *Reaction vessel.*

the helium or the chlorine could bypass the calorimetric vessel. The exit gases were passed through a trap cooled with liquid nitrogen to collect the excess chlorine and the titanium tetrachloride vaporized during the experiment.

4. Procedure

A sample (0.2 to 0.4 g) of titanium was weighed into the quartz crucible and the vessel assembled and placed in the calorimeter can with 1,855 g of water. The air and moisture were removed as completely as possible from the vessel by successive evacuation and filling with purified helium.

The calorimetric temperature observations were divided into three periods, a 60-min reaction period and two 20-min rating periods, one immediately preceding and the other following the reaction period. Temperatures were observed at 1-min intervals during the reaction period and at 2-min intervals during the rating periods [3].

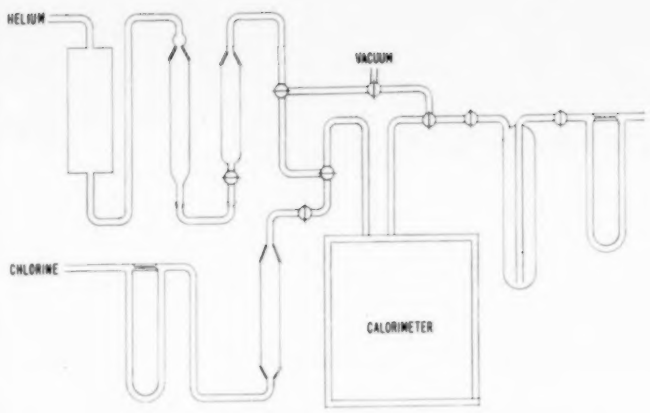

FIGURE 2. *Gas train.*

Chlorine was introduced into the vessel at the start of the reaction period, and the vessel was heated electrically. When the desired rise in temperature was obtained, the electric current was interrupted, the flow of chlorine stopped, and helium was introduced into the vessel to flush out the remaining chlorine. The helium was allowed to flow for about 30 min and then stopped. An additional 10 min was allowed for thermal equilibrium to be re-established, after which temperatures were observed during the final rating period.

The rates of flow of chlorine and helium were determined by means of calibrated capillary flowmeters; the total quantities were determined from the rate and time of flow. The temperature of the helium and chlorine was assumed to be the same as that of the calorimeter jacket through which they passed. These data were required only for calculation of the small correction for the heat carried into the calorimeter by the chlorine and helium.

The quantity of reaction was determined from the mass of sample, since the reaction was complete in all cases. The liquid $TiCl_4$ remaining in the vessel was flushed out with helium and the quantity determined by analysis [4]. These data were used to correct the results for the heat of vaporization of the portion of the liquid that did not vaporize during the experiment. The contents of the trap were also analyzed for $TiCl_4$; this served as a check on the amount of reaction.

After all the $TiCl_4$ was flushed out, the vessel was disassembled, and the crucible was removed and weighed. No correction was made for the very slight residue, the mass of which was always less than 1 mg.

The calorimetric system was calibrated in exactly the same manner except for omission of the titanium and chlorine. In each case the quantity of electrical energy was carefully measured and the initial and final temperatures of the calorimeter reproduced as closely as possible. This is known as the substitution method of calorimetry, in which the energy associated with a known quantity of a given chemical reaction is directly compared with electrical energy in terms of calibrated standards.

5. Results and Calculations

The results of the electrical calibration experiments are given in table 1, in which E_e is the electrical energy added to the system, ΔRc is the corrected temperature rise expressed in ohms, q_g is a correction to 25° C for the heat capacity of the helium, and E_s is the energy equivalent of the system in joules per ohm.

The results of the calorimetric experiments are given in table 2. The quantity q is the total energy absorbed by the calorimeter, obtained as the product of E_s and ΔRc. The apparent heat of the chemical reaction, q_r, is obtained as the difference between q and E_e. The quantity q_g is a correction to 25° C for the heat capacities of the reactants, products, and the helium; the quantity q_v is a correction for the vaporization of the titanium tetrachloride remaining in the vessel after the experiment.

TABLE 1. *Results of the electrical calibration experiments*

Experiment No.	E_e	q_g	ΔRc	E_s
	j	*j*	*Ohm*	*j/ohm*
1	29564.8	20.1	0.354054	83560.4
2	29343.7	18.7	.351368	83565.9
3	28454.1	19.2	.340776	83554.3
4	29161.9	11.1	.349191	83544.8
5	28043.6	9.7	.335833	83533.5
Mean				83551.8
Standard deviation of mean				±5.8

TABLE 2. *Results of the calorimetric experiments on titanium tetrachloride*

Experiment No.	ΔRc	q	E_e	q_r	q_g	q_v	Ti	$-\Delta H(25° C)$
	Ohm	*j*	*j*	*j*	*j*	*j*	*Moles*	*kj/mole*
1	0.329287	27512.5	24432.2	3080.3	−9.5	−38.5	0.0039944	759.14
2	.363176	30344.0	27562.4	2781.6	−8.5	−25.1	.0035962	764.14
3	.399533	33381.7	29497.0	3884.7	−2.1	−48.8	.0049891	768.44
4	.348517	29119.2	25262.4	3856.8	−7.3	−77.0	.0049418	763.39
5	.345635	28878.4	26180.8	2697.6	−10.7	−24.9	.0034975	761.12
6	.352348	29439.3	24309.2	5130.1	−7.7	−158.4	.0065039	763.23
Mean								763.24
Standard deviation of mean								±1.28

The heat of vaporization of titanium tetrachloride was taken as 9.9 kcal/mole from the calorimetric measurements of Schaffer, Breil, and Pfeffer [5]. The density of titanium was taken as 4.50 g/cm^3 [6]. The heat of reaction obtained in joules per mole was converted to the conventional thermochemical calorie by the following relationship:

$$1 \text{ cal} = 4.1840 \text{ j}.$$

The mean value for the heat of formation given in table 2 corresponds to the following reaction:

$$\begin{aligned} &Ti_{(c)} + 2Cl_{2(g)} = TiCl_{4(g)}, \qquad (1)\\ &\Delta Hf°(25°C) = -763.2 \pm 2.9 \text{ kj/mole}\\ &\qquad\qquad = -182.4 \pm 0.7 \text{ kcal/mole}. \end{aligned}$$

Another series of five experiments was performed on samples taken from a sheet of commercial titanium obtained from the Titanium Metals Corporation of America. The manufacturer furnished the following analyses in percent: Ti, 99.74; C, 0.019; N_2, 0.047; Fe, 0.08; and O_2, 0.17. The heat of formation corresponding to reaction (1) obtained for samples from this sheet was −764.0 ±2.1 kj/mole (−182.6 ±0.7 kcal/mole).

A single experiment was also carried out using a sample of sponge titanium obtained from the Bureau of Mines (courtesy of David Schlain). The heat of formation obtained was −763.6 kj/mole (−182.5 kcal/mole).

The uncertainties assigned to the values given in this paper were obtained by combining twice the standard deviation of the mean of the calibration and reaction experiments with reasonable estimates of all other known sources of error.

Combination of (1) with the heat of vaporization of $TiCl_4$, 9.9 kcal/mole, gives the heat of formation of liquid $TiCl_4$.

$$\begin{aligned} &Ti_{(c)} + 2Cl_{2(g)} = TiCl_{4(liq)}, \qquad (2)\\ &\Delta Hf°(25° C) = -804.6 \pm 2.9 \text{ kj/mole}\\ &\qquad\qquad = -192.3 \pm 0.7 \text{ kcal/mole}. \end{aligned}$$

6. Discussion

After vaporization of the liquid titanium tetrachloride from the vessel, there was usually a very small, reddish deposit remaining in the bulb of the vessel. This material was nonvolatile and was soluble in the liquid tetrachloride. It was not possible to remove any of this material because of its small quantity and its tendency to adhere to the vessel. It was, therefore, dissolved by washing with 5 percent sulfuric acid and the quantity determined by analysis. The quantity of Ti was found to be not more than 0.25 percent of the original sample. Although the composition of the substance is not known, the titanium present has been assumed to be in the form of an oxide or an oxychloride of titanium. The heat of formation of titanium dioxide is −225.7 kcal/mole [7] and that of $TiOCl_2$ has been estimated to be −205 kcal/mole. In view of this information it would appear that the maximum error in the heat of formation of $TiCl_4$ caused by production of this material would be less than 0.1 kcal/mole which is well within the uncertainty ascribed to the value given in this paper.

Two samples of the $TiCl_4$ produced in the reaction were examined by means of the mass spectrometer. The analyses showed that the material was free from $SiCl_4$ but contained some of the fluorocarbon stopcock grease. There was no evidence of reaction between the grease and the $TiCl_4$ vapors; it appears, however, that liquid $TiCl_4$ reacts slowly with the grease resulting in the displacement of one or more chlorine atoms with fluorine. There was no contact of liquid $TiCl_4$ with the grease in the calorimeter; the contact was made during the analysis.

The emission spectrograph analysis of one of the

samples of $TiCl_4$ obtained from the commercial titanium gave 0.0015 percent Si, 0.0010 percent Ni, 0.0005 percent Sn, 0.0005 percent Al, and a total of 0.0009 percent of other metals. This analysis was performed by Martha Mayo Darr of the Spectrochemistry Section of the Chemistry Division. If these impurities are assumed to be present as chlorides, the error in the measured heat of formation due to these materials would amount to less than 0.01 percent.

Prior to this investigation, calculations of the heat of formation of $TiCl_4$ were based on the experimental data obtained by Thomsen for the heat of hydrolysis [8]. He reported the results obtained for the following reaction at 18° C:

$$TiCl_{4(liq)}+2H_2O_{(liq)}\longrightarrow 4HCl_{(aq,\ 0.002M)}+TiO_{2(rutile)},$$
$$\Delta H=-57.9 \text{ kcal/mole.}$$

Thomsen reported that when the HCl produced in the reaction was titrated with NaOH only 47.7 kcal was evolved instead of the 55.0 to be expected from the neutralization of 4 moles of dilute NaOH at 18° C. This has caused considerable confusion in the use and interpretation of his results.

From Thomsen's data Roth and Becker [9] calculated the heat of formation of liquid $TiCl_4$ to be −185 kcal/mole. Rossini, Wagman, Evans, Levine, and Jaffe [10] give −179.3 kcal/mole for the heat of formation of $TiCl_4$ at 25° C based also on Thomsen's primary data.

Humphrey [7] has determined the heat of formation of TiO_2 to be −225.7 kcal/mole by combustion in an oxygen bomb. From this value for the heat of formation of TiO_2, the accepted values [10] for the heats of formation of water and aqueous hydrochloric acid, and the corrected value obtained by Roth and Becker for Thomsen's heat of hydrolysis, the heat of formation of $TiCl_{4(liq)}$ at 25° C is calculated to be −194.7 kcal/mole. An error of 4 percent in Thomsen's value for the heat of hydrolysis of $TiCl_4$ could explain the discrepancy between his value and that obtained in the present investigation. In view of the uncertainty in the states of the hydrolysis products, this is highly probable.

Since the completion of this investigation, there have been reported four independent determinations of the heat of formation of titanium tetrachloride.

Farber and Darnell [11] studied the equilibrium.

$$TiO_{2(rutile)}+4HCl_{(g)}=TiCl_{4(g)}+2H_2O_{(g)},$$

in the temperature range of 800 to 1,400° K. Their data lead to −192.5 ±0.5 kcal/mole for the heat of formation of liquid $TiCl_4$ at 25° C.

Skinner and Ruehrwein [12] measured the heat of formation directly by carrying out the reaction of titanium with chlorine under pressure and obtained −190.3 ±3.0 kcal/mole.

Gross, Hayman, and Levi [13] measured the heat of the reaction of titanium with liquid chlorine and the heat of solution of the tetrachloride in chlorine. Using 4.406 kcal/mole for the heat of vaporization of the chlorine, they obtained −191.5 ±0.3 kcal/mole for the heat of formation of $TiCl_{4(liq)}$.

Krieve, Vango, and Mason [14] measured the heats of formation of $TiCl_{4(liq)}$ by carrying out the reaction of $Ti_{(s)}$ with $Cl_{2(gas)}$ under pressure in a nickel bomb. They obtained −190.0 ±0.4 kcal/mole for the heat of formation under standard conditions.

A comparison of the experimental values is given in the following tabulation:

Farber and Darnell	−192.5 ±0.5,
Skinner and Ruehrwein	−190.3 ±3.0,
Gross, Hayman, and Levi	−191.5 ±0.3,
Krieve, Vango, and Mason	−190.0 ±.4,
This investigation	−192.3 ±.7.

It should be emphasized that the value obtained in this investigation is independent of the heat of vaporization of chlorine and of any heats of solution which may introduce additional errors.

7. References

[1] E. J. Prosen, W. H. Johnson, and F. Y. Pergiel, J. Research NBS **62,** 43 (1958) RP2927.
[2] E. J. Prosen, F. W. Maron, and F. D. Rossini, J. Research NBS **46,** 106 (1951) RP2181.
[3] J. R. Eckman and F. D. Rossini, J. Research NBS **3,** 597 (1929) RP111.
[4] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, Applied inorganic analysis, 2d ed., p. 518 (John Wiley and Sons, Inc., New York, N. Y., 1953).
[5] H. Schaffer, G. Breil, and G. Pfeffer, Z. anorg. allgem. Chem. **276,** 325 (1954).
[6] J. D. Fast, Z. anorg. allgem. Chem. **241,** 42 (1939).
[7] G. L. Humphrey, J. Am. Chem. Soc. **73,** 1587 (1951).
[8] J. Thomsen, Thermochemische Untersuchungen, I (Verlag J. A. Barth, Leipzig, 1882).
[9] W. A. Roth and G. Becker, Z. Physik. Chem. [A]**159,** (1932).
[10] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, Selected values of chemical thermodynamic properties, NBS Circ. **500** (U. S. Government Printing Office, Washington 25, D. C., 1952).
[11] M. Farber and A. J. Darnell, J. Chem. Phys. **23,** 1460 (1955).
[12] G. B. Skinner and R. A. Ruehrwein, J. Phys. Chem. **59,** 113 (1955).
[13] P. Gross, C. Hayman, and D. L. Levi, Trans. Faraday Soc. **53,** 1601 (1957).
[14] W. F. Krieve, S. P. Vango, and D. M. Mason, J. Chem. Phys. **25,** (3) 519 (1956).

WASHINGTON, D. C., August 19, 1958.

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